ULTRAVIOLET SPECTROSCOPY OF INORGANIC SOLIDS

by

FREDERICK FORBES, A.H.-W.C.

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University of Edinburgh.

ABSTRACT OF THESIS

Name of Candidate Frederick Forbes

Address

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Title of Thesis Ultraviolet spectroscopy of inorganic solids.

The factors affecting the reflectance of an absorbing substance mixed with material not absorbing at the wavelength of measurement were investigated, and it was found that the effect of particle size could be eliminated by prolonged grinding. It is shown that the percentage by weight of an absorbing substance is directly proportional to the quantity $(\frac{A}{R})^{1.383}$ (R = percentage reflectance; A = 100 - R) and that this quantity is additive for two absorbing substances. A method is developed for the accurate determination of low concentrations of one and two absorbing substances mixed with a non-absorbing substance. However, since the spectra of inorganic compounds are dependent on their previous history the method is only applicable for mixtures from a similar source, or which have undergone similar treatment, to the standards. The method is not applicable if there is physical interaction between the components of the mixture.

The reflectance method of quantitative analysis of solid mixtures is applied to the determination of the composition of the solid products formed in solid/solid inorganic reactions: the principles involved are analogous to those used by Job in solution spectrophotometry. The method was tested by applying it to several MoO_3/basic oxide systems which had been previously studied by other techniques and then applied to other MoO_3/basic oxide systems hitherto not investigated or on which controversy exists. In all cases confirmation was obtained by a parallel x-ray powder diffraction study. For reactions involving the oxides of the non-transition metals the compositions of the products formed can be located within very narrow limits by the reflectance method and this becomes /

Use other side if necessary.

becomes of greatest importance when dealing with compounds of an unbalanced composition (a compound formed from unusual molar proportions of reactants, e.g. 7:5 or 12:1). For reactions involving the transition metal oxides the reflectance method is not applicable and this is related to the nature of the spectra involved in these cases.

To my parents and my wife.

CONTENTS

INTRODUCTION

This section falls into two parts: the first is a survey of diffuse reflectance spectrophotometry with particular reference to mixtures of solid substances, and the second is a review of the methods available for the determination of the composition of products formed in solid state reactions.

The radiation reflected by a finely powdered solid consists of two components: a diffuse part, the radiation penetrating the interior and re-emerging after being scattered numerous times, and a regular part arising from the reflection at the surface of single crystallites. If the solid shows selective absorption then a portion of the incident radiation is absorbed, and a spectrum can be obtained from the study of the intensity of the reflected radiation at a series of wavelengths. Reliable reflectance spectra were first obtained by Pfund (1920, 1923) who illuminated the powder surface with radiation from a mercury lamp; the reflected light, after passing through a spectrograph was collected on a photographic plate and the percentage radiation reflected at various wavelengths obtained by comparison with MgO.

Karl (1934) suggested characterising inorganic compounds from their reflectance spectra, and this was developed by Billy and Berton ($1938_{a, b, c}$) who studied a large number of compounds. These workers regarded the reflectance spectrum as a superimposition of the pure reflectance spectrum and the absorption spectrum by transmission, but it was shown experimentally that the light reflected by internal diffusion, as well as being a function of the absorption coefficient k, is also a function of the scattering or diffusion coefficient S (Amy, 1937)

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The theory of Kubelka and Munk (1931) has been frequently used to relate the diffusely reflected light to these coefficients; it is assumed that the light enters a medium containing optical inhomogeneities, which are incomparably smaller than the thickness, and which are uniformly distributed in the medium. An integration is made over infinitesimally thin planes and results in equation (1)

$$R\ diff_{\infty} = \left(\frac{I}{I_o}\right)_1 = \frac{1 - \sqrt{\frac{k}{k + 2S}}}{1 + \sqrt{\frac{k}{k + 2S}}} \qquad \ldots\ldots\ldots\ldots \quad (1)$$

which by transformation gives

$$F(R)_{\infty} = \frac{(1 - R_{\infty})^2}{2\,R_{\infty}} = \frac{k}{S} \qquad \ldots\ldots\ldots\ldots \quad (2)$$

For the regular part, according to the Laws of Fresnel, the reflectance is given by:-

$$R(reg) = \left(\frac{I}{I_o}\right)_2 = \frac{(n - 1)^2 + n^2 K^2}{(n + 1)^2 + n^2 K^2} \qquad \ldots\ldots\ldots \quad (3)$$

This holds only for the most simple case of normal incidence. n represents the refractive index of the medium and K, the absorption index, is proportional to k being given by $\frac{k \lambda_o}{4\pi n}$.

From equation (3) it can be seen that for large values of K, R(Reg) approachs the limiting value of unity; that is highly absorbing substances possess high reflectivity so that diffuse and regular reflectance counteract one another. Spurious maxima in diffuse reflectance spectra can result from this, but by reducing the particle size, the contribution of regular reflectance is /

is diminished and the structure of the reflectance spectrum is improved (Kortüm and Schöttler, 1953).

There are two methods of eliminating the regular reflectance. The first, used by Amy (1937) and recently by Makas (1962) requires the use of plane polarised radiation: the portion which is internally scattered suffers depolarisation, whereas the regularly reflected portion does not and can therefore be removed. The second (Kortüm and Schreyer, 1955) is to adsorb the test substance on an adsorbent which has been preheated to remove any contaminants which may block the interaction. Since reflectance measurements are taken relative to the adsorbent, the regular reflection is essentially the same in both cases, and is therefore eliminated.

The second procedure has been the more widely used. Providing that a complete monomolecular layer of the material under investigation is not present on the adsorbent then the Kubelka-Munk relationship was found to hold (Kortüm and Schreyer, 1956). Replacing the molar absorption coefficient k in equation (2) by 2·303 e.c., where e is the extinction coefficient and c the molar concentration of the adsorbed substance then,

$$F(R)_\infty \propto \frac{e.c.}{s} \quad \ldots\ldots\ldots\ldots\ldots\ldots (4)$$

Working at constant grain size it was found that the Kubelka-Munk function $F(R)_\infty$ was proportional to the concentration of the adsorbed substance; this was used to determine concentration of adsorbed species in column chromatography (Kortum and Schreyer, 1956). The scattering coefficient was found to vary inversely with the particle size of the adsorbent, so that reduction in particle size decreases the sensitivity (Kortum et al., 1953, 1963); the scattering coefficient /

coefficient was also found to be nearly independent of wavelength, except with very fine particles (Kortüm et al. 1963), so that when Log F $(R)_\infty$ is plotted against wavelength a "typical colour curve" of the adsorbed species is obtained (Kortüm, 1957). Due to Van der Waals adsorption forces the reflectance spectrum is broadened, the bands are displaced to longer wavelengths and the vibrational structure, if present at all, is strongly suppressed (Kortüm et al., 1963). In certain cases, strong interaction corresponding to chemisorption occurs between the adsorbent and the adsorbate and leads to correspondingly large changes in the reflectance spectrum; deviations of the Kubelka-Munk function from ideality in these cases have been used to calculate the dissociation constant of the adsorbed molecular compound (Kortüm and Braun 1958).

Other equations relating the diffuse reflectance to the absorption coefficient have been derived. One of these takes into account multireflected rays, particle size, index of refraction and also Rayleigh Scattering (Johnston 1952). In another complex approach, the reflectance from a powdered sample, is calculated, without assuming parallel homogeneous layers, on an individual particle basis (Melamed, 1963); this approach has been applied to the study of the spectra of chromia-alumina solid solutions (Poole and Itzel, 1963).

A comprehensive study of the factors influencing the diffuse reflectance of mixtures of solids in which discrete particles are present, as opposed to those in which adsorption occurs, has not bee n reported. Strongly absorbing species have been diluted with lithium fluoride to obtain reliable absorption maxima (Griffiths et al., 1959). Lermond and Rogers (1955) investigated the possibility of using reflectance measurements as a means of analysing solid mixtures /

mixtures but, though they state that screening procedures are essential, the effect of varying particle size was not reported. The mixtures investigated were mainly of ferric oxide in barium sulphate; the variation of reflectance with concentration did not follow the Kubelka-Munk function and another plot, that of Log R-Rm against the square root of the concentration of Fe_2O_3, where Rm is thereflectance of the sample having the highest concentration in the series, gave approximately linear variation. Fischer and Vratny (1955) made a similar study of ferric oxide in magnesium carbonate and report that the plot of 100-% reflectance against Log % Fe_2O_3 was linear; neither particle size employed nor wavelength employed are given. They report that mixtures containing more than one coloured component are quite complex and that no useful analytical means of interpreting the reflectance readings was possible, but no details are given. Two papers have been published (Baistrocchi, 1959); Rubinchik, 1963) in which the reflectance method is applied to a kinetic study of the ferric oxide-alkaline earth oxide system, in which the ferrite is formed. The degree of reaction was estimated by determining the ferric oxide from its visible absorption, and also by an independent chemical extraction method. Use was made of the Kubelka-Munk function in the spectrophotometric method, though its applicability to such systems was not illustrated in either case. Nevertheless, Baistrocchi obtained excellent agreement between the two methods as shown in Table 1.

Table 1.

% Fe_2O_3 reacted	Spectrophot.	2·4	5·0	14·1	27·5	43·1
	Chemical	2·1	4·5	15·0	28·4	43·3

These results were obtained by subtraction of the Fe_2O_3 present after reaction from the amount originally present. Since in most cases these two quantities are of the same magnitude the accuracy must have been high by both methods to obtain significent results. Assuming no error was incurred in the chemical method the accuracy of the spectrophotometric method must be appreciably better than 0·5%; the previously best claimed accuracy for diffuse reflectance is 2-3% (Kortüm and Haug, 1953) and this was for systems in which the Kubelka-Munk function had been shown valid. Rubinchik, on the other hand, studied the reaction when it was nearing completion and his results are given in Table 2.

Table 2.

% Fe_2O_3 not reacted									
	Spectrophot.	24.0	21·7	19·2	15·3	14·9	13·8	10·6	7·3
	Chemical	27·6	24·0	20·0	15·8	12·6	10·0	6·5	4·9

At low concentrations of Fe_2O_3 the results are relatively high by the reflectance method when the Kubelka-Munk function is used. This is in keeping with the findings of Lermond and Rogers (1955). It was decided, therefore, to investigate more fully the reflectance of mixtures of two or more substances with a view to developing a general analytical technique.

The x-ray method and the chemical extraction method have been the most widely used in the determination of the composition of the products of solid state reactions, which involve no volatile products.

The application of x-ray powder techniques to the detection of crystalline solids in powder mixtures has been a very important factor in the determination of/

of the composition of products of solid state reaction. For example, the composition of both the intermediate and final products in the solid state reaction between CaO, Al_2O_3 and SiO_2 have been determined by photographic procedures (Jander and Petri, 1938). Recently a counting diffractometer was applied to the study of theproducts formed in the solid state reaction between $KHSO_4$ and K_2SO_4 (Silber and Avinems, 1963). The outstanding disadvantage of x-ray methods is their dependance on the crystallinity of the material. The presence of poorly crystallised material hinders the detection of crystalline phases, particularly when present in small amounts. Another disadvantage is that even in cases of good crystallinity it is often difficult to detect less than 5% of a component, at least by photographic methods (Bunn, 1945).

In certain cases the composition of the product can be determined by separating it from an excess of a reactant, making use of their differing solubilities in a suitable solvent. This method has been used to determine the composition of the product in a reaction involving MoO_3 and a basic oxide (Zelikman and Belyaevskaya, 1954). The procedure, however, is only of limited applicability since for many systems suitable solvents cannot be found and in addition there is always the possibility that the product will undergo reaction with the solvent.

Other techniques such as differential thermal analysis, infrared spectroscopy and magnetic susceptibility have been used to show the occurrence of a reaction in a given system, but, presumably because they are relatively insensitive to small changes in composition, they have not been generally applied on a quantitative basis to determine the composition of reaction products. In the present work the application of diffuse reflectance spectroscopy to such studies is investigated.

I. Analysis of Solid Mixtures by Diffuse Reflectance Spectrophotometry.

Kortum has investigated the factors influencing the diffuse reflectance of solid mixtures but, as his studies were restricted to cases in which one of the substances is physically adsorbed on the surface of the other, and to mixed crystals, his findings were of little use in this work where mechanical mixtures were investigated. It was necessary, therefore, to make a preliminary study of the experimental variables influencing the quantitative reflectance of such mixtures and in this section the development of a procedure for obtaining reproducible reflectance measurements for a given mixture is described. The variation of % absorption with the percentage of the absorbing species in the mixture was studied and it was found that the relationship $W = K \left(\frac{A}{R}\right)^{1.383}$ (where A, R are the % absorption and % reflectance respectively, W is the percentage of the absorbing species and K is a constant for a given system) held within experimental error over a wide concentration range, whereas the relationships used by Kortum, Lermond and Rogers (1955), Fischer and Vratny (1955) did not. For the quantitative analysis of a mixture of two solids an accuracy of 6% was obtained. The method was extended to the quantitative analysis of mixtures of three solids and an accuracy of 6% was again obtainable.

I. A. Influence of Experimental Variables.

A Unicam S.P. 500 spectrophotometer with an S.P. 540 diffuse reflectance attachment was used for all diffuse reflectance measurements. The systems studied were mixtures of two solids, one of which was not absorbing and the other having a maximum in absorption, in the wavelength region of study. The reflectance measurements were taken relative to the substance not absorbing in the mixtures at two wavelengths, one the wavelength of maximum absorption and the other a wavelength at which neither component absorbed. The effect of the spectrophotometric variables, of the method of preparation of the test and standard surfaces, and of the particle size has been investigated.

In the Unicam S.P. 540 diffuse reflectance attachment, the light scattered by the sample is collected by a narrow, ring shaped, spherical mirror which reflects the light on to the photocell. Only light diffusely scattered over a narrow angular range is collected and is compared with the light reflected from a reference, non-absorbing, substance whose surface is similarly prepared. As only a relatively small proportion of the incident light is collected, it is necessary to work at slit widths larger than those used in solution spectrophotometry. At 330mμ the maximum slit width must be employed, and at shorter wavelengths the sensitivity of the photocell must be increased in order to obtain a balance. At wavelengths shorter than 270mμ the sensitivity is so high that the reflectance of the test surface cannot be read with reliability to 1% in reflectance. This deficiency has been overcome with the use of a photomultiplier (Griffith etal., 1959) but in the present work all measurements were confined to the range 270 - 1000mμ .

Numerous /

Numerous methods of preparing the matt surfaces, which should be uniformly flat and have identical packing characteristics, were attempted. The most satisfactory found was to arrange the sample in a heap in the holder and use a rubber bung to remove excess material and to smooth the surface, care being taken not to compress the sample in the holder.

The materials used in the series of experiments were silver iodide and zinc oxide which have absorption maxima (reflectance minima) at 425mμ and 368mμ respectively, and magnesium oxide and silicic acid which do not absorb in the range investigated. All substances were ground in an agate mortar and passed through a 200 mesh (B.S.) sieve. Adequate mixing of two components was achieved by shaking a total of 4g. in a 1 oz. bottle for 2 hours on a vibrational shaker. The reflectances of the mixtures were measured, in all cases, relative to the component which was non-absorbing in the range investigated.

The effect of surface variations on reflectance measurements were studied. In the first instance, the relative reflectances of several magnesium oxide surfaces were compared; one magnesium oxide surface was kept fixed and the other freshly prepared for each measurement, but despite preparing the surfaces in an apparently identical manner, the reflectances from the two surfaces were generally slightly different, the variable surface reflecting between 96 - 104% of the light reflected from the fixed surface. This effect seems to be due to the packing of the sample as surfaces prepared by compression with the rubber bung gave abnormally high reflectances. In addition to this the reflectance was often slightly wavelength dependent, a change of 0·2 - 0·5% reflectance being common over a wavelength range of 300mμ . When uneven surfaces were prepared, this effect became more pronounced, and is therefore at least partly due to differences in the geometry of the surfaces.

The /

The effect of varying the reference surface on the measured reflectance of a permanent ZnO - MgO surface was examined at 368mμ , the wavelength of maximum absorption of ZnO, and also at 450mμ , at which wavelength it does not absorb. The reflectance at 368mμ was found to vary but only in proportion to the reflectance measured at 450mμ as is shown in Table 3.

Table 3.

Reflectances of a 1% ZnO - MgO Mixture.

$R._{450m\mu}$	$R._{368m\mu}$	$\frac{R._{368m\mu}}{R._{450m\mu}}$
101·7	77·8	76·5
100·6	77·2	76·7
100·7	76·6	76·1
98·4	75·5	76·7
95·8	73·2	76·4
104·0	80·4	77·3
102·0	78·0	76·5
98·2	75·4	76·8

The reflectances were, therefore, whenever possible taken relative to a reflectance measured in the region of no absorption. The corrected reflectances, will however, be subject to an error resulting from the wavelength dependence of different surfaces but as this error is small, correction for this was not attempted.

It was found more convenient to use % absorption, defined as 100- % reflectance after correction.

The repeatability of the % absorption on varying the surface of a given sample, and the reproducibility of the % absorption for mixtures of the same composition were investigated. The results obtained for four magnesium oxide mixtures, /

mixtures, each containing 3·00 % zinc oxide by weight are shown in Table 4. For each sample four different test surfaces were measured relative to a permanent magnesium oxide reference surface at 368mμ .

Table 4.

Repeatibility and Reproducibility of Reflectance Measurements

	Mixture			
Surface	1	2	3	4
1	56·2	59·1	55·8	58·2
2	57·7	57·5	55·6	55·6
3	56·6	55·8	56·4	55·2
4	59·1	56·2	58·4	54·4
Mean	57·4	56·7	56·5	55·9

The % absorption is repeatable to ± 2%, and whenthe average % absorption of four surfaces is taken, the reproducibility is ± 1% in absorption. In all subsequent work the results quoted are for an average of the measurements on three to five surfaces.

The effect of particle size on the absorption was examined. Silver iodide was ground in an agate mortar and sieved through the following B.S. sieves:- 100, 120, 140, 160, 180, 200, 250 and 300, thus obtaining fractions between narrow sieve limits. Mixtures of each fraction with magnesium oxide were prepared containing 9·00% silver iodide by weight. The % absorption was measured at 425mμ, the wavelength of maximum absorption of silver iodide, and the results are shown in Table 5.

Table 5.

Effect of particle size on Absorption.

Sieve Fraction	% Absorption
100 - 120	8.0
120 - 140	8.8
140 - 160	8.8
160 - 180	11.7
180 - 200	10.7
200 - 250	16.4
250 - 300	14.7
passing 300	30.5

Reduction in the particle size of silver iodide gives rise to an increase in the % absorption but attempts to prepare silver iodide of smaller particle size failed due to the tendency of the fine particles to bind together to form glass-like flakes. The particle size of the magnesium oxide also influences the % absorption.

It was found that the influence of the particle size on the absorption could be eliminated by grinding the mixtures in an agate mortar for about 15 minutes, since further grinding was found to produce no further increase in absorption. Table 6 shows the results obtained on grinding the silver iodide-magnesium oxide mixture, containing the silver iodide passing 300 mesh, for various times.

Table 6.

Effect of Grinding on Absorption

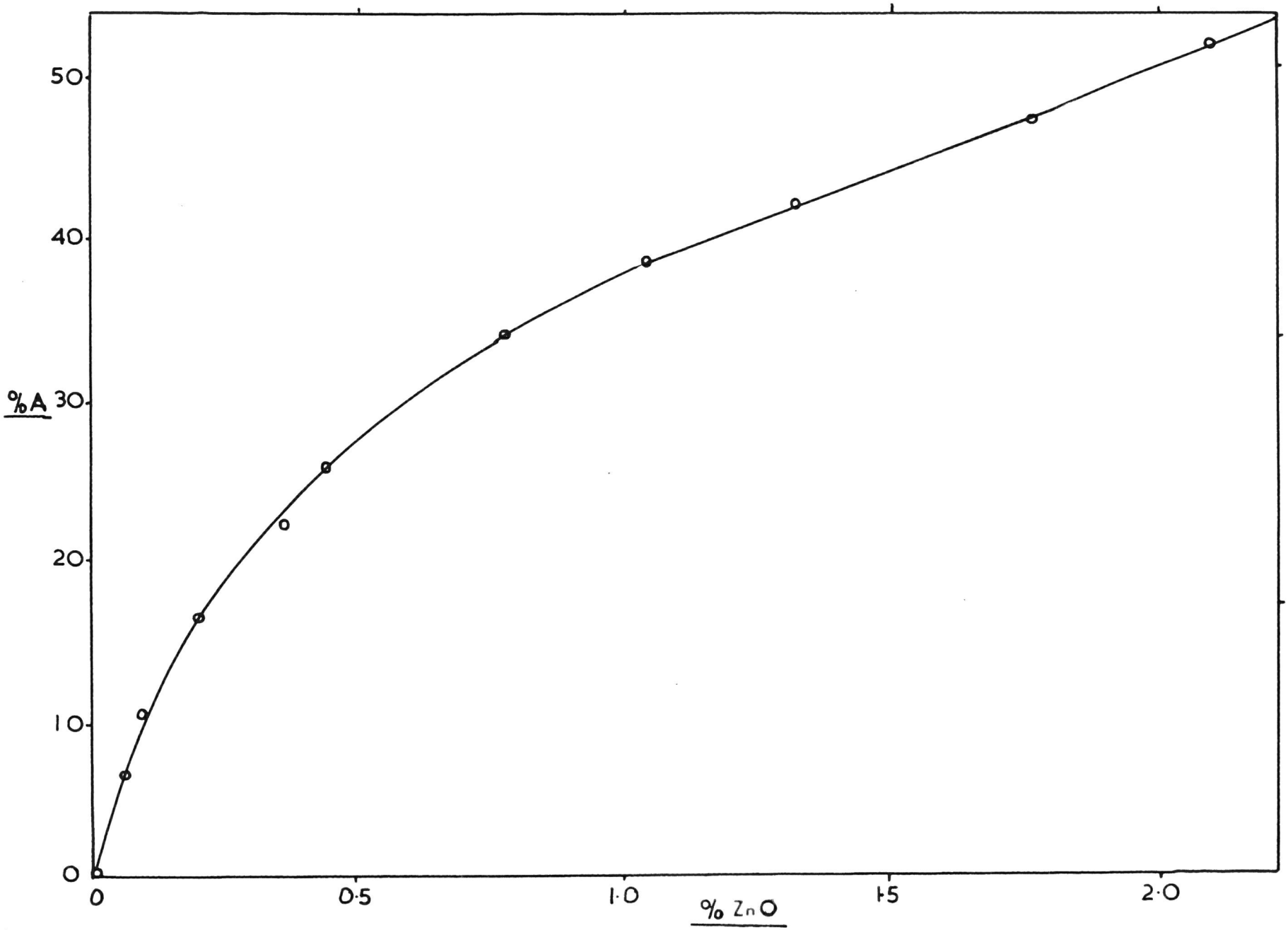
Time of Grinding (Minutes)	% Absorption
0	30·5
2	50·2
5	69·1
8	73·0
10	76·4
12	78·3
14	76·5
16	77·1
20	76·8
30	76·6

The limiting absorption was found to be independent of the initial particle size ranges. Other mixtures, for example ZnO - silicic acid, were also found to give limiting absorptions on grinding. In this procedure it is important that the reference substance is treated in an analogous manner so that its surface is analogous to that of the test surface.

An average of four measurements, after a limiting absorption had been obtained, was found to be repeatable to 1% in absorption which is the same repeatibility obtained for unground mixtures.

FIGURE 1

PLOT OF % ABSORPTION AGAINST % ZnO



I. B. Analysis of Two Component Systems.

The variation of % absorption with concentration was investigated for several systems of mixtures of two components and an absorption function which varies linearly with concentration is proposed. The results are applied to the analysis of mixtures of two solids and compared with the x-ray powder diffraction method.

The two component systems studied are shown in Table 7.

Table 7.

Systems Investigated.

System	State of Mixture	No. of Mixtures
ZnO - MgO	passing 200 mesh	12
AgI - MgO	"	8
ZnO - silicic acid	"	7
ZnO - Al_2O_3	"	7
ZnO - MgO	limiting absorption	13
AgI - MgO	"	6
PbO - MgO	"	6
PbO - silicic acid	"	8
ZnO - silicic acid	"	7
ZnO - Al_2O_3	"	7

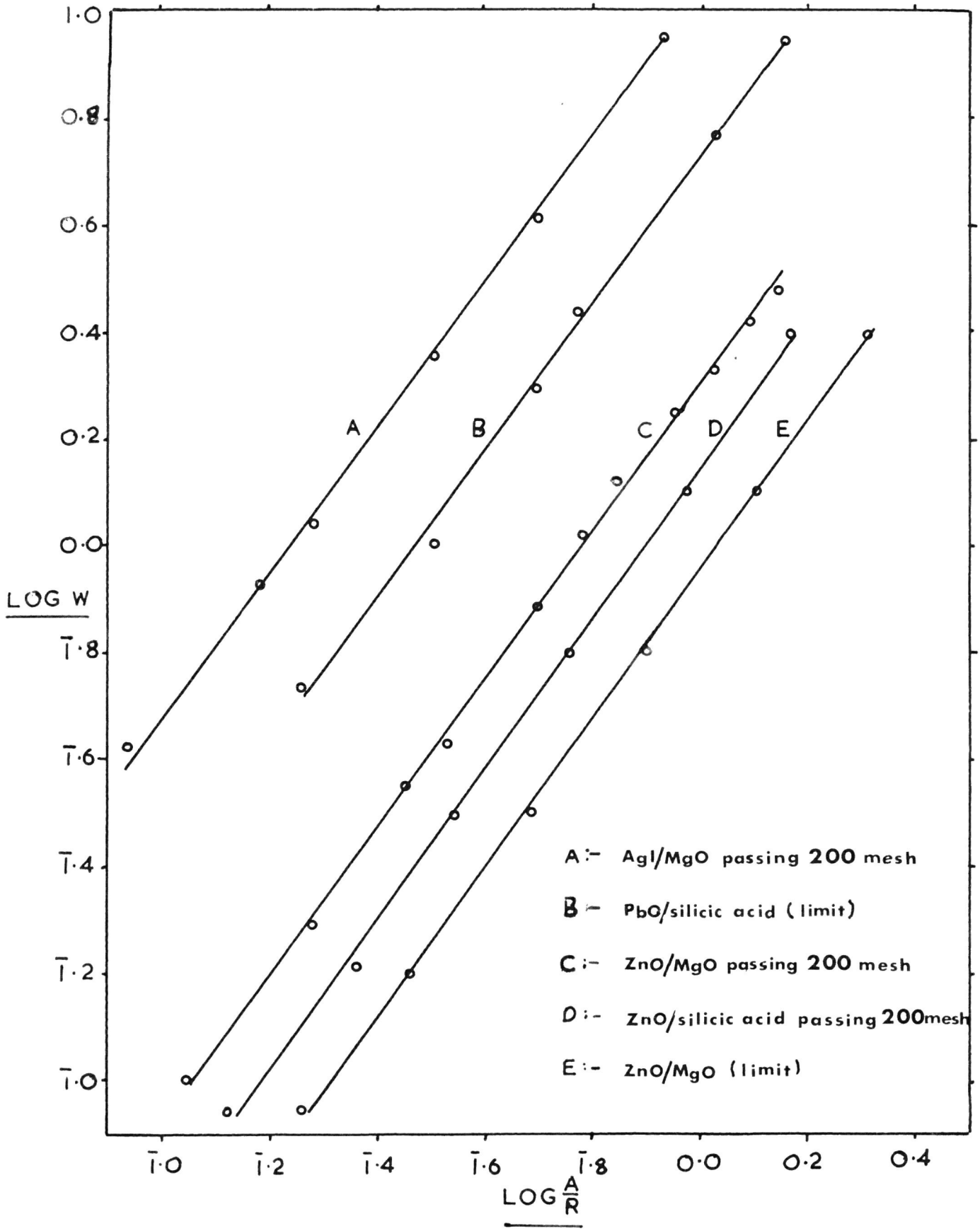
In all cases reflectance measurements were taken at the wavelength of maximum absorption, which for ZnO, AgI and PbO is 368, 425 and 515 mμ respectively. These reflectances were scaled relative to a reflectance in the region of no absorption and the % absorption obtained as previously described. For each mixture four surfaces were prepared and an average of the results taken.

Regular variation of absorption with concentration was observed in all cases and Fig. 1 shows the plot obtained for the zinc oxide - MgO mixtures.

Mixtures /

FIGURE 2

PLOT OF LOG W AGAINST LOG $\frac{A}{R}$



Mixtures subjected to the grinding procedure absorbed more strongly than mixtures of larger particle sizes of the same composition, except in the case of ZnO/Al_2O_3 where the absorption decreased. Other differences of this system were observed and these are discussed at the end of this section.

For the results obtained in this study the plots suggested by Fischer and Vratny ($_{1955}$) and Lermond and Rogers ($_{1955}$) approached linearity only over a narrow range of reflectance. The Kubelka-Munk plot, used by Kortüm, approximated to linearity over the range 40 - 60% reflectance, but deviated widely outside these limits. Numerous empirical relationships were tested for linearity: the plot of Log $\frac{A}{R}$ against Log W. where W is the percentage of the species absorbing at the wavelength of measurement, was found to show linearity for all mixtures studied, excepting of course, the ZnO - Al_2O_3 mixtures. The plot for several systems is shown in Fig.2 from which it follows that

$$\text{Log } W. = n \text{Log } \frac{A}{R} + \text{Log } K \quad \ldots\ldots\ldots\ldots\ldots\ldots \quad (1)$$

where n is the slope of the line and K is a constant for a given system

$$\therefore \quad W = K \left(\frac{A}{R}\right)^n \quad \ldots\ldots\ldots\ldots\ldots\ldots \quad (2)$$

Further, as is seen from Fig.2 the plots are parallel within experimental error, showing that n is independent of the system studied. Table 8 shows the values of K and n obtained.

Table 8.

Values of n and K for the Systems Investigated.

System	State of Mixture	n	K
ZnO - MgO	passing 200 mesh	1·355	1·984
AgI - MgO	"	1·366	10·96
ZnO - silicic acid	"	1·396	1·355
ZnO - MgO	limiting absorption	1·400	0·763
AgI - MgO	"	1·378	1·152
PbO - MgO	"	1·385	3·85
PbO - silicic acid	"	1·380	5·42
ZnO - silicic acid	"	1·396	0·863

The mean value of n is 1·383 and this was used in all subsequent work, the expression becoming $W = K\left(\frac{A}{R}\right)^{1.383}$ . . . . . (3)

To illustrate the applicability of this equation over wide ranges in concentration, the values of K for the ZnO - MgO mixtures passing 200 mesh was calculated from the reflectance results and are shown in Table 9; included are analogous results by the Kubelka-Munk treatment.

Table 9.

Calculated Value of K.

% ZnO	% Absorption	$K = W/\left(\frac{A}{R}\right)^{1.383}$	$W/\left(\frac{1-R}{2R}\right)^{2}$
3·185	58·4	1·99	7·78
2·654	55·3	1·98	7·76
2·093	51·5	1·94	7·66
1·756	47·0	2·06	8·42
1·214	41·4	1·97	8·28
1·038	37·9	2·08	8·94
0·7715	33·5	1·98	9·40
0·431	25·4	1·91	10·0
0·355	21·8	2·09	11·6
0·196	16·1	1·90	12·5
0·098	10·2	1·92	12·2
0·056	6·3	2·33	26·6

These results show that the equation derived holds over far wider concentration ranges than does the Kubelka-Munk function. The most accurate region was found to be from 30-70% absorption; outside this region a small error in measurement causes a comparatively large error in $(\frac{A}{R})^{1.383}$.

For the quantitative analysis of mixtures of two solids only the limit absorption measurements, which are not dependent on initial particle size, were taken. To calculate the percentage of a constituent present, use was made of equation (3), which holds accurately at the wavelength of maximum absorption, over the absorption range 30-70%.

The accuracy which can be obtained was determined for a number of ZnO/MgO mixtures, prepared by an independent operator, all of which gave absorption readings in the 30-70% range. The mixtures were ground until the absorption at 368 mμ did not change with further grinding, and then a mean of the absorptions for four differing test surfaces taken in each case. The percentage ZnO was calculated using the equation $\%ZnO = 0.763\ (\frac{A}{R})^{1.383}$ which was obtained from the previous limit calibrations and the results are given in Table 10.

Table 10.

Accuracy of Reflectance Method.

% ZnO	
Actual	Found
0.140	0.130
1.12	1.225
0.59	0.562
0.81	0.83
0.70	0.70
0.73	0.77
1.18	1.11

The standard deviation from the actual percentage is 6·4%.

The linearity of theabsorption function with concentration has been illustrated for several systems at the wavelength of maximum absorption, $\lambda_{MAX.}$. That this linearity holds at all wavelengths λ was deduced from a study of the spectra of two component mixtures.

It has been shown that

$$W = K_{\lambda_{MAX}} \left(\frac{A}{R}\right)^{1.383}_{\lambda_{MAX}} \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \quad (3)$$

and if this relationship holds at all other wavelengths it follows that

$$\frac{\left(\frac{A}{R}\right)^{1.383}_{\lambda}}{\left(\frac{A}{R}\right)^{1.383}_{\lambda_{MAX}}} = \frac{K_{\lambda_{MAX}}}{K_{\lambda}} = \text{a constant} \ldots\ldots\ldots \quad (4)$$

The procedure followed was to measure the reflectance spectra of mixtures of differing concentration after grinding to a limiting absorption, and after converting the measured reflectances to $\left(\frac{A}{R}\right)^{1.383}$ values in all cases, to compare the ratio of the absorption function at any wavelength to that at the wavelength of maximum absorption for mixtures of differing percentage. To minimise calculation, a series of plots of % reflectance against equivalent $\left(\frac{A}{R}\right)^{1.383}$ were drawn up and used for the conversions. Measurements for four silicic acid mixtures containing 42,3·02, 5·00 and 7·82% PbO gave the results shown in Table 11. The mean results are given, together with the maximum deviations.

Table 11.

mμ	$(\frac{A}{R})^{1.383}_{\lambda} / (\frac{A}{R})^{1.383}_{368m\mu}$	mμ	$(\frac{A}{R})^{1.383}_{\lambda} / (\frac{A}{R})^{1.383}_{368m\mu}$
1000-800	0	542	0·814 ± 0·016
750	0	540	0·854 ± 0·018
675	0	535	0·922 ± 0·019
650	0·0007 ± 0·0002	530	0·962 ± 0·008
625	0·0062 ± 0·0032	525	0·987 ± 0·004
600	0·015 ± 0·003	520	0·995 ± 0·005
590	0·024 ± 0·004	515	1·000
585	0·032 ± 0·005	510	1·000
580	0·049 ± 0·006	500	0·987 ± 0·005
575	0·078 ± 0·007	490	0·966 ± 0·006
570	0·128 ± 0·008	480	0·942 ± 0·006
568	0·155 ± 0·013	470	0·920 ± 0·003
566	0·189 ± 0·020	460	0·900 ± 0·014
564	0·226 ± 0·017	450	0·886 ± 0·014
562	0·266 ± 0·017	440	0·868 ± 0·007
560	0·318 ± 0·033	430	0·847 ± 0·010
558	0·372 ± 0·034	420	0·834 ± 0·007
556	0·431 ± 0·032	410	0·818 ± 0·013
554	0·492 ± 0·037	400	0·799 ± 0·019
552	0·557 ± 0·034	390	0·771 ± 0·006
550	0·616 ± 0·036	380	0·737 ± 0·004
548	0·681 ± 0·035	370	0·702 ± 0·021
546	0·734 ± 0·036	368	0·682 ± 0·025
544	0·781 ± 0·031	360	0·668 ± 0·019
		350	0·633 ± 0·023

It is concluded that the ratio of the absorption at any wavelength to that at the wavelength of maximum absorption is virtually independent of the % PbO. This establishes the validity of equation (4) for this system, and hence that the absorption function $(\frac{A}{R})^{1.383}$ varies linearly with concentration at all wavelengths. Analogous conclusions were drawn from a study of four mixtures of silicic acid containing 0·040, 0·162, 0·317 and 2·55% ZnO.

The effect of the second component on the spectrum of ZnO was examined. A number of substances were taken, all of which were shown to be non-absorbing in the region studied by comparing their reflectance with that of pure MgO, and /

and mixtures with ZnO prepared. After grinding to a limiting absorption the reflectance spectrum was measured in each case and the ratios of the absorption at several wavelengths to that obtained at 368 mμ were compared. Typical comparative results are shown in Table 12.

Table 12.

mμ	MgO	silicic acid	$AlPo_4$	$CaCo_3$	$Al_2(SiO_4)_3$	$MgCo_3$	Al_2O_3
390	0·017	0·002	0·006	0·009	0·007	0·005	0·159
384	0·034	0·044	0·053	0·072	0·054	0·042	0·322
378	0·436	0·390	0·432	0·424	0·418	0·420	0·670
375	0·764	0·717	0·744	0·720	0·744	0·741	0·858

The ratio of the absorption at any wavelength to that at the wavelength of maximum absorption is virtually independent of the second component, except in the case of alumina , showing that the spectrum of the zinc oxide is not generally affected by the second component. The alumina-zinc oxide system is later discussed.

X-ray powder photographyis the common method of detecting a compound in a mixture of solids; the sensitivity of this technique was compared with that of diffuse reflectance. A Unicam 9 cm. camera was used for taking all x-ray powder photographs and with this camera the film is mounted by the Van Arkel method in which the beam comes through the centre of the film, low angles of diffraction being observed at the edges of the film and high angles at the middle region. A Cu K_α source, in conjunction with a Ni filter, was used giving radiation of wavelength 1·5404 Å. The sample was contained in a capillary

capillary lithium borate glass tube and in most cases an exposure time of 20 minutes was found suitable. The positions of the diffraction lines were measured with a steel rule and converted to d spacings; the intensities of the lines were estimated visually and expressed relative to the strongest which was arbitrarily taken as 100. The limit of detection of a substance in a mixture of solids was arbitrarily defined as the smallest percentage of the species which shows two of its diffraction lines.

In diffuse reflectance spectrophotometry an absorption of 0·5% is significent, but less than this may be attributable to errors in measurement and errors resulting from the wavelength dependence of the surface studied; the limit of detection was therefore defined as the percentage of the species in the mixture which shows 0·5% absorption, at the wavelength of maximum absorption.

Several systems were studied and the results obtained by both methods are shown in Table 13.

Table 13.

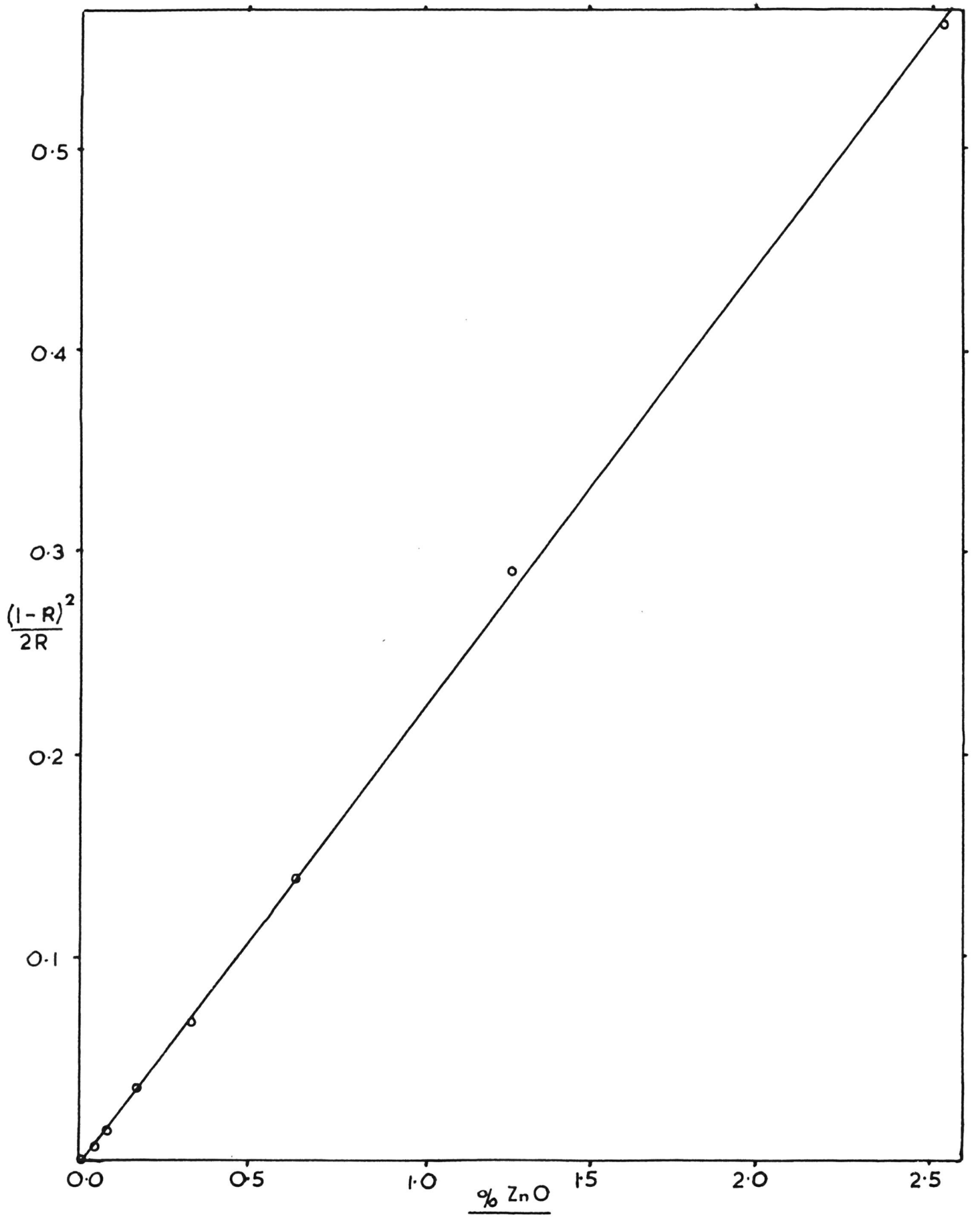
Comparison of X-ray and Reflectance Methods.

System A - B	Limit of Detection of A	
	Reflectance	X-ray
AgI - MgO	0·002%	2%
ZnO - MgO	0·001%	1%
ZnO - Silicic acid	0·002%	2%
PbO - MgO	0·008%	2%
PbO - Silicic acid	0·010%	2%

The reflectance method for the systems studied is 200-1000 times more sensitive that the x-ray method. There are, however, superior methods for obtaining x-ray powder photographs and measuring diffraction line intensities and /

FIGURE 3

KUBELKA-MUNK PLOT FOR ZnO/Al_2O_3



and positions. For example, a focusing camera gives much sharper lines and a densitometer (or a counting diffractometer) as well as allowing a more accurate estimation of line intensities, can detect lines of low intensity when the background of the photograph is diffuse.

Peculiarities of the $ZnO-Al_2O_3$ system have been previously referred to. A thorough investigation of this system revealed the following:-

(i) Mixtures ground to a limiting absorption absorb less radiation than those of a discrete particle size range: this is the opposite observed for other systems.

(ii) The relationship $\%ZnO = K(\frac{s}{k})^{1.383}$ does not express the variation of the absorption with concentration and the Kubelka-Munk function was found valid as is apparent from the plot in Fig. 3.

(iii) The spectrum of ZnO was altered when in admixture with Al_2O_3. When in the presence of other second components the ZnO had an absorption maximum at 368-9mμ compared with 370mμ in alumina; the onset of absorption was 410-425mμ for other components but for alumina it was 450mμ. These differences correspond to a bathochromic shift of the ZnO spectrum and further evidence for this was previously given in Table 12.

Kortüm has shown that in cases where one component is physically adsorbed on the other, reduction of particle size gives rise to a decrease in absorption; the Kubelka-Munk function holds for finely ground particles; and bathochromic shifts are observed in the spectrum of the adsorbed substance. It is concluded, therefore, that ZnO is physically adsorbed on alumina.

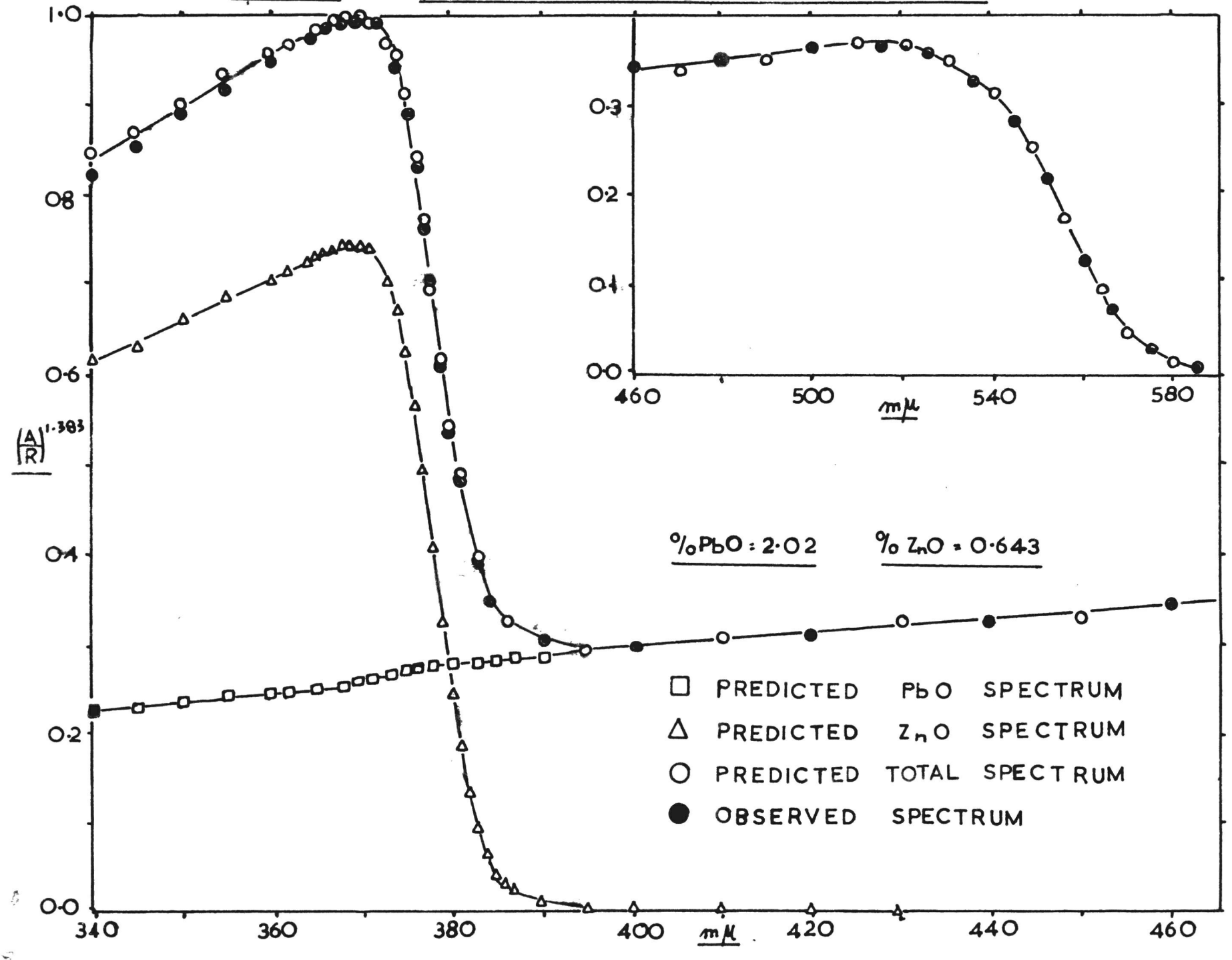
I. C. Analysis of Three Component Mixtures.

The analysis of three component systems is simplified by choosing wavelengths for measurements at which differing components absorb exclusively, but in the solid mixtures studied this was not possible. For example, in the PbO - ZnO - silicic acid system, the PbO and ZnO have absorption maxima at 515mμ and 368mμ respectively and though only the PbO absorbs at its maximum the absorption extends into the ultraviolet and no region exists in which the ZnO alone absorbs. However, from spectral studies of three component mixtures, it is shown that the spectra of PbO and ZnO are additive at all wavelengths, and as a result allowance for the PbO absorption in the ultraviolet is possible, leaving that due only to ZnO. Estimation of both constituents is therefore possible and the accuracy found by studying several mixtures of known composition was 6%. The ratio of PbO to ZnO found in these mixtures was accurate to 3% and use was made of this in developing an improved method of analysis of two component mixtures based on the internal standard principle.

The additivity of the PbO and ZnO spectra was examined in the region 340 - 1000mμ . Three mixtures containing differing percentages of PbO and ZnO in silicic acid were prepared and the limit reflectances measured. These reflectances were scaled in the usual way, so that the reflectance in the region of no absorption was 100% and then converted to $(\frac{1}{R})^{1.383}$ equivalents. In each case, these absorptions were compared with those predicted, which were calculated in the following way:- from the percentage of PbO present, the absorption expected at 515mμ was calculated from the value of K previously obtained for the PbO - silicic acid system, and at other wavelengths from the data obtained in the spectral study as previously given in Table 11. The absorption expected for ZnO at 368mμ and at other wavelengths, was calculated in the same way.

These /

FIGURE 4 ADDITIVITY OF PbO AND ZnO SPECTRA



These absorptions due to PbO and ZnO were summed giving the total predicted absorptions.

These predicted absorptions, agreed very well with those measured in all cases showing that the ZnO and PbO spectra are additive at all wavelengths. The predicted and observed absorptions are shown for one of the mixtures in Fig. 4.

In the analytical studies, measurements were taken at 515mμ and 368mμ. At the first of these the PbO was estimated using the equation 5, which is based on calibrations for the PbO - silicic acid system.

$$\% \text{ PbO} = 5{\cdot}42 \left(\frac{A}{R}\right)^{1{\cdot}383}_{515m\mu} \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots (5)$$

At 368mμ both PbO and ZnO absorb. An accurate value of the ratio of the PbO absorption at 368mμ to that at 515mμ was obtained by measurement of a large number of PbO - silicic acid mixtures, the results being shown in Table14.

Table 14.

Ratio of PbO Absorptions.

% PbO	$\left(\frac{A}{R}\right)^{1{\cdot}383}_{368m\mu} / \left(\frac{A}{R}\right)^{1{\cdot}383}_{515m\mu}$
0·543	0·667
1·002	0·679
1·981	0·687
2·762	0·675
4·059	0·701
5·795	0·718
8·88	0·698

The mean ratio is 0·689 with a standard deviation of 0·018.

The absorption due to PbO at 368mμ is therefore 0·689 times that measured at 515mμ. The absorption of the ZnO at 368mμ is governed by the equation /

equation % ZnO = $0{\cdot}863(\frac{A}{R})^{1{\cdot}383}_{368m\mu}$ and since the absorptions of ZnO and PbO are additive it follows that

$$(\frac{A}{R})^{1{\cdot}383}_{368m\mu} = 0{\cdot}689(\frac{A}{R})^{1{\cdot}383}_{515m\mu} + \frac{\%ZnO}{0{\cdot}863}$$

and $\therefore$ $\%\ ZnO = 0{\cdot}863\ \left((\frac{A}{R})^{1{\cdot}383}_{368m\mu} - 0{\cdot}689\ (\frac{A}{R})^{1{\cdot}383}_{515m\mu} \right)$ . . . . . (6)

Measurements at 368mμ and 515mμ were made on a number of mixtures of known composition to determine the accuracy of the method. Rather than study mixtures of random composition, two series were prepared, one in which the ratio of PbO to ZnO was maintained constant and the other in which the percentage ZnO was maintained constant. The ranges in composition were chosen to give all measurements in the accurate range, 30-70% absorption. The percentages of PbO and ZnO, calculated using equations (5) and (6) are compared with those actually present in Table 15.

Table 15.

Results for Three Component Mixtures.

% PbO		% ZnO	
Actual	Found	Actual	Found
6·980	7·15	3·054	3·26
5·927	5·69	2·595	2·62
4·949	5·22	2·164	2·29
3·938	4·08	1·723	1·87
2·898	2·82	1·268	1·28
1·906	1·99	0·834	0·863
7·650	8·24	1·543	1·71
3·861	4·10	1·475	1·58
3·199	2·98	1·509	1·49
2·017	2·11	1·487	1·62
0·982	1·01	1·487	1·55
0·538	0·563	1·445	1·53

The standard deviation from the actual percentages is 6·6% for the ZnO and 5·2% for the PbO. These results are of the same order of accuracy as was obtained for the analysis of twocomponent systems. Accurate estimation of the ZnO will not, however, be possible when the absorption due to PbO at 368mμ is large compared to that due to ZnO, and the limit of detection of the ZnO in the mixture will also depend on the percentage of PbO present.

The ratio of the percentages of PbO to ZnO found in these mixtures is compared with the actual ratio present in Table 16.

Table 16.

Ratios of % PbO to % ZnO.

% PbO	%PbO / % ZnO	
	Actual	Found
6·980	2·24	2·19
5·927	2·24	2·17
4·949	2 ·24	2·27
3·938	2·24	2·13
2·898	2·24	2·19
1·906	2·24	2·30
7·650	4·97	4·82
3·861	2·62	2·60
3·199	2·12	2·00
2·017	0·968	0·948
0·982	0 ·660	0·658
0·538	0·372	0·368

The standard deviation from the actual ratio is 3·2%. It was found from studying surfaces differently packed, that though the absorption at a given wavelength changed appreciably with the degree of packing, the ratio of the absorptions at two wavelengths remained approximately constant; this accounts for the more accurate results obtained for the ratio of percentages. Use was made /

made of this improved accuracy in an internal standard method for the analysis of mixtures of two solids:- to the mixture is added a known weight of a third substance and, from absorption measurements at suitable wavelengths, the ratio of the added substance to one of the components in the mixture calculated; knowing the percentage of the added substance the percentage of the component in the mixture is calculated.

Mixtures of PbO in silicic acid were prepared by an independent operator. To each was added a known weight of zinc oxide and the absorption at 515mμ and 368mμ measured in the usual way. The percentage PbO was calculated from these measurements using relationship (7), which was obtained by the combination of equations (5) and (6)

$$\% \text{ PbO} = \% \text{ ZnO} \quad \frac{6.33 \left(\frac{A}{R}\right)^{1.383}_{515m\mu}}{\left(\frac{A}{R}\right)^{1.383}_{368m\mu} - 0.689 \left(\frac{A}{R}\right)^{1.383}_{515m\mu}} \quad \ldots\ldots \quad (7)$$

The results obtained were corrected to allow for the weight of ZnO added and are shown in Table 17.

Table 17.

Results for Internal Standard Method.

% PbO	
Actual	Found
1.47	1.50
6.14	6.41
2.92	3.01
2.78	2.82
2.58	2.48
2.70	2.60
2.93	2.78
2.81	2.66

The standard deviation from the actual percentage is 4·0%. This is better than the direct method for which an accuracy of 6% is obtainable but, save for cases where the highest accuracy is required, the additional time spent is probably not justified.

II. The Study of Solid State Reactions by Diffuse Reflectance Spectrophotometry.

In the study of solid state reactions reliable conclusions are generally drawn on the basis of a comparison of the results obtained by the use of different methods of investigation. In the present study use was made of the reflectance method of analysis of solid mixtures, and of x-ray investigations. In the reflectance study, since both products and reactants absorb very strongly at the wavelengths of maximum absorption, the reacted mixtures were diluted with magnesium oxide, which does not absorb in the wavelength region studied, in order to obtain measurements in the range over which the absorption function is most accurate. The measurements were taken relative to a reference magnesium oxide surface so that the procedure was strictly analogous to that used in the investigation of solid mixtures.

For each system a comparison of the reflectance spectra and x-ray powder photographs, obtained before and after heating a mixture of the reactants, indicated whether reaction had occurred or not.

The determination of the composition of the product formed by diffuse reflectance methods, was complicated by the fact that frequently both reactants and products absorbed at the wavelengths most suitable for study, though, of course, to differing extents; it was not, therefore, generally possible to estimate the excess of a reactant in a reacted mixture from a measured absorption, and so deduce the composition of the product. Indirect procedures, based on Job's continuous variations method (Job, 1928) were devised and these are discussed later.

The validity of the reflectance method was established by the study of several MoO_3/ basic oxide systems, all of which had been previously studied in the solid state/

state, and then applied to a number of other MoO_3 systems not previously studied. The compositions of the products were verified in both cases by the x-ray method. The principles of the reflectance method hold for systems in which more than one product is formed and the results obtained for such systems are reported.

II. A. Method of Investigation.

In this work, precautions are necessary to ensure that spectral changes are due to reaction and not to changes in the reactants brought about by heating. Further, in the determination of the composition of a product, it is essential that all mixtures studied are completely reacted.

The colour, and hence the spectrum of inorganic oxides, is frequently altered by thermal treatment; there are several reasons for this, but, for example, the change may be due to a polymorphic transformation as for PbO (yellow and red forms), or a small change in stoicheiometry as for NiO (green or black). In this study complications arising from possible changes were avoided by pretreatment of the reactants. The oxides were separately heated overnight to the temperature at which reaction was to be studied. Heating for longer periods was unnecessary as the spectra did not change further. A detailed study of the spectral changes which accompany the heating of CuO is reported in Section III.

The conditions used for carrying out the reaction were chosen to give completion in as short a time as possible. The reactants were mixed and ground together in an agate mortar for exactly 15 minutes, and good contact was obtained by pelleting the mixture in a Perkin-Elmer 13mm. K Br die at a pressure of 10 tons, under vacuum, for exactly 2 minutes. In general, the higher the temperature used the greater is the rate of reaction but, in the systems studied,

an/

an upper limit was imposed since the volatility of MoO_3 becomes appreciable at temperatures well below the m.p. of 795°. The relative volatility at different temperatures was estimated by heating 1g. pellets of MoO_3 for 24 hours and the results are shown in Table 18.

Table 18.
Loss in Wt. of MoO_3 at different temperatures

Temp.	Loss
600°	< 0.0002g.
640°	< 0.0002g.
660°	0.0004g.
680°	0.0006g.
700°	0.0010g.
720°	0.0040g.
740°	0.0190g.

The volatility becomes significant above 700° and this was used as the upper temperature limit in the studies. This procedure did not completely suffice as, after heating for 24 hours, the pellets were often not completely reacted. The reaction was accelerated by grinding the pellets after short heating intervals, which allowed the unreacted materials to come in contact, repelleting and reheating. This procedure was carried out twice, three heating intervals of 2, 4 and 12 hours being used. Further treatment was shown to be unnecessary in most cases as no changes in the spectrum occurred on heating for another interval. The samples were heated in a small electric muffle furnace and the temperature was controlled by a Gallenk amp on/off controller. The accurate temperature in the vicinity of the sample was measured by an additional chromel/alumel thermocouple in conjunction with a Doran thermocouple potentiometer, and/

and showed a variation of $\pm 4^{\circ}$ from the mean at 700° due to the controller cycle. For a given series the pellets were stacked in a platinum crucible and were separated from one another by platinum foil; this ensured similar temperature and heating intervals for mixtures of differing composition.

The determination of the composition of the product was determined by a process, analogous to Job's continuous variations method which is widely used in spectrophotometry to determine the composition of products formed between reactants in solution. In Job's method, a series of solutions of the reactants are prepared in which the mole fraction of one of the reactants is continuously varied from 0 to 1, but the total molar concentration is maintained constant. The optical densities measured are compared with those that would have been obtained had no reaction occurred, and the greatest difference results for the solution whose composition is nearest that of the product. In cases where negligible dissociation of the product occurs, the plot of this difference in optical density ($\Delta O.D.$) against composition gives two straight lines, which intersect at the composition of the product. Job's method depends on the additivity of optical density. For solid state reactions a similar procedure using $(\frac{A}{R})^{1.383}$ should hold over the range in which the absorption function is additive. In this case a constant number of moles of reacted mixtures of various compositions would be diluted to constant weight with MgO. The validity of this analogy was established as follows:-

Consider two reactants A and B which combine to give a product Am Bn

i.e. $mA + nB \longrightarrow Am\ Bn$

Suppose that in a series of mixtures a total of one mole of reactants is commenced with. Let the number of moles of A be represented by X, then the number of moles of B is 1 -X. After reaction the mixtures are diluted to a suitable/

suitable constant weight with MgO. At the wavelength of measurement let the absorptions due to 1 mole of A, B, and Am Bn be Za, Zb, and Zp respectively. Providing the absorption is expressed in terms of $(\frac{A}{R})^{1.383}$ it will be additive.

Before reaction, the absorption (A_1) expected will be given by:-

$$A_1 = xZ_a + (1-x)\,Z_b \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (1)$$

After reaction either A or B will be in excess.

With A in excess:

Since $mA + nB \longrightarrow Am\,Bn$

then $xA + (1-x)B \longrightarrow \frac{1-x}{n}\,Am\,Bn + (x - \frac{m}{n}(1-x))\,A$

The absorption (A_2) after reaction will be given by:-

$$A_2 = \frac{1-x}{n} Z_p + (x - \frac{m}{n}(1-x))\,Z_a \quad \ldots\ldots\ldots\ldots\ldots\ldots (2)$$

Subtracting (1) from (2) the difference in absorption ($\triangle A$) before and after reaction is obtained.

$$\triangle A = \frac{1-x}{n} Z_p - (\frac{m}{n}(1-x))\,Z_a - (1-x)\,Z_b \quad \ldots\ldots\ldots\ldots\ldots (3)$$

With B in excess:

Similarly it can be shown, when B is in excess, that the absorption (A_3) after reaction is given by:-

$$A_3 = \frac{x}{m} Z_p + ((1-x) - \frac{n}{m} x)\,Z_b \quad \ldots\ldots\ldots\ldots\ldots\ldots (4)$$

and the difference is absorption ($\triangle A$) by:-

$$\triangle A = \frac{x}{m} Z_p - (\frac{n}{m} x)\,Z_b - x\,Z_p \quad \ldots\ldots\ldots\ldots\ldots\ldots (5)$$

The variation of $\triangle A$ with x is obtained by differentiation

$$\text{A in excess } \frac{d(\triangle A)}{dx} = \frac{-Z_p}{n} + \frac{m}{n} Z_a + Z_b \quad \ldots\ldots\ldots\ldots\ldots (6)$$

$$\text{B in excess } \frac{d(\triangle A)}{dx} = \frac{Z_p}{m} - \frac{n}{m} Z_b - Z_a \quad \ldots\ldots\ldots\ldots\ldots (7)$$

Since Z_a, Z_b, Z_p, m and n are constants it follows that the variation is linear in both cases. A plot of $\triangle A$ against x will give two straight lines. For a reacted /

reacted mixture whose composition is identical to that of the product formed both equations are valid, since the excess in each case is zero, and the lines must intersect at this composition.

An alternative procedure is the direct plot of absorption against composition; variation is again linear since differentiation of A_2 and A_3 (equations (2) and (4)) yield constants

$$\frac{dA_2}{dx} = -\frac{Z_p}{n} + Z_a\left(1 + \frac{m}{n}\right) \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \quad (8)$$

$$\frac{dA_3}{dx} = \frac{Z_p}{m} - Z_b\left(1 - \frac{n}{m}\right) \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \quad (9)$$

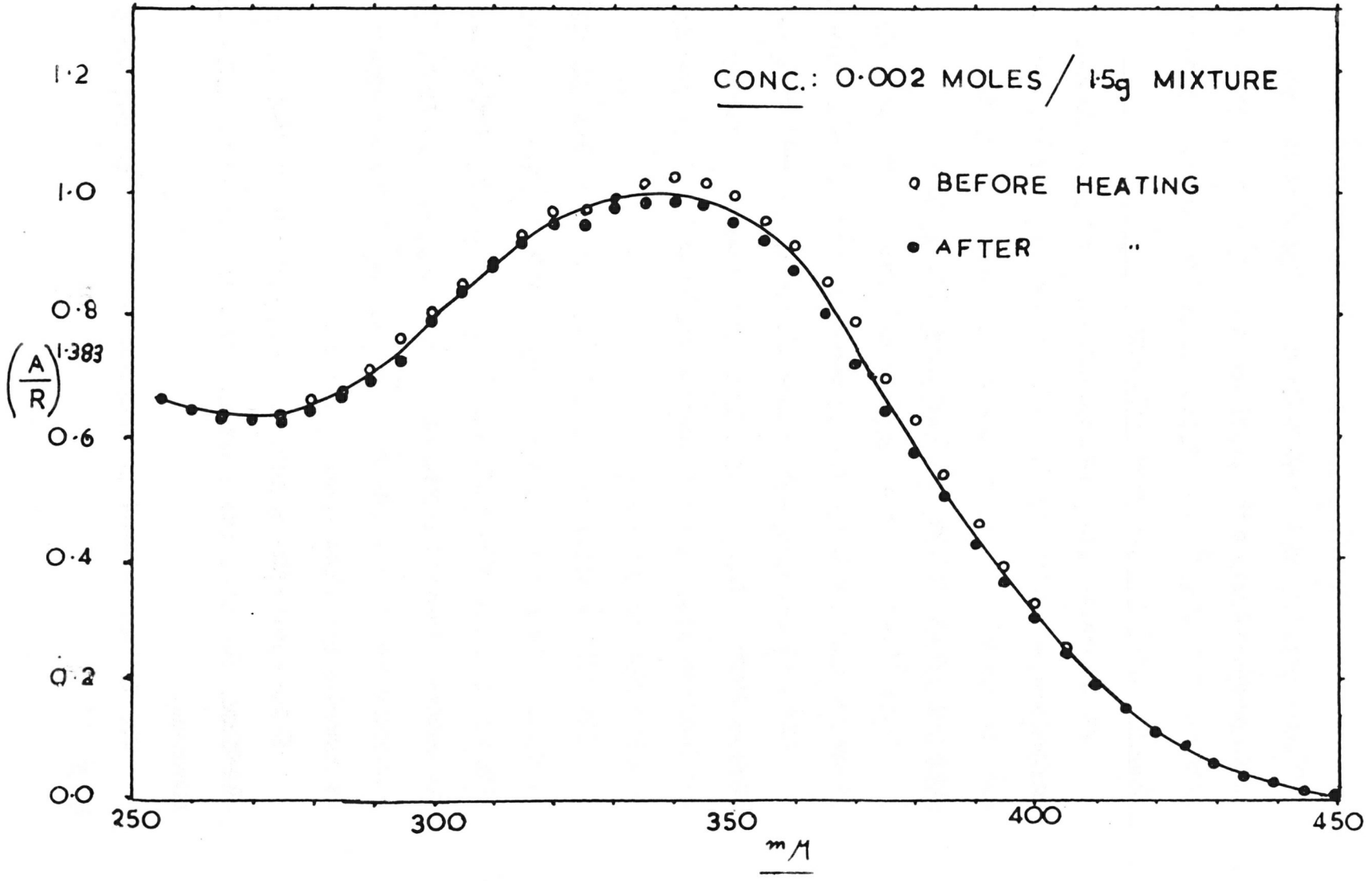
These lines must again intersect at the composition of the product, since equations (2) and (4) are valid for this composition.

In general this second procedure was used since less calculation is involved but in several instances Job's plots are given.

For systems in which more than one compound is formed it can be shown by analogous treatment that maxima or minima in absorption will be observed at the composition of every product.

FIGURE 5

SPECTRUM OF MoO_3/SiO_2



II.B. Systems Previously Studied.

The ability of MoO_3 to react in the solid state with the following oxides:- ZnO, CdO, MgO, CoO, NiO and CuO has been previously reported. For each system the compound formed has been reported as the normal molybdate though the evidence for this, in some cases, is not conclusive. With SiO_2 it is reported that no reaction takes place with MoO_3.

In this work, these systems were studied by the diffuse reflectance techniques, described in the previous section, to test their applicability and also by the x-ray method to supply confirmatory evidence.

Reaction between Silica and Molybdenum Trioxide:

Duval (1952), by comparing the infrared absorption spectra before and after heating, concluded that no reaction takes place between MoO_3 and SiO_2.

The SiO_2 and MoO_3 were separately heated at 700° overnight and then a mixture (SiO_2 : MoO_3 = 1:2 molar) was prepared: a portion of this was retained and the remainder, after pelleting, was heated to 700° overnight. No visual colour change was apparent.

The diffuse reflectance spectrum of the heated and unheated mixtures was obtained. In each case, a dilution of 0.00200 moles to a total weight of 1.500g. with MgO gave reliable reflectance readings after grinding to a limiting absorption. The readings were taken relative to pure magnesium oxide which had been ground for a similar time. The spectra, shown in Fig. 5, were identical suggesting that no reaction had taken place on heating.

X-ray powder photographs of the heated and unheated mixtures were identical, all lines being due only to SiO_2 and MoO_3, confirming the absence of reaction.

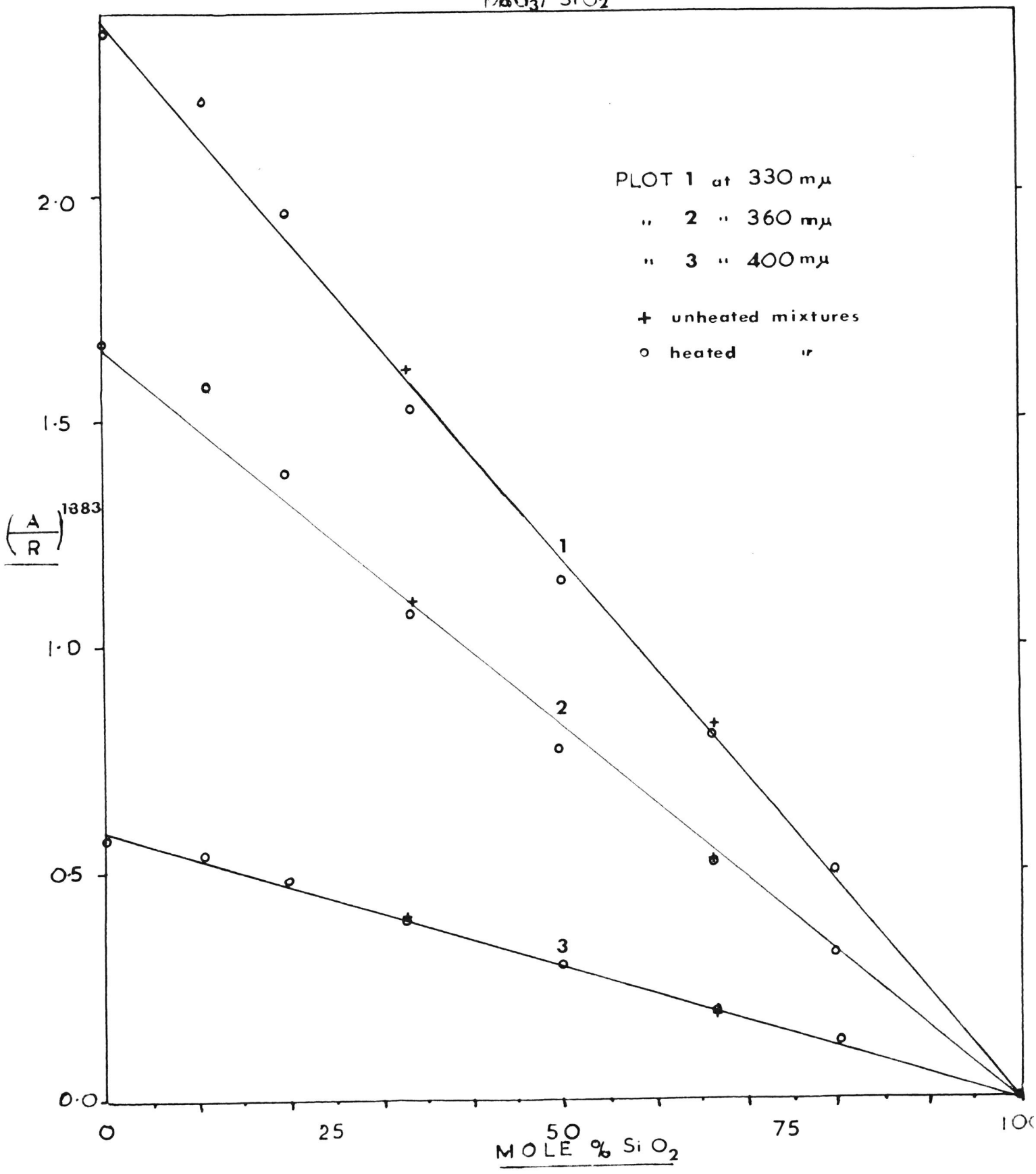
For systems in which no reaction occurs composition/absorption plots should

be /

FIGURE 6

ABSORPTION PLOTS FOR

Nb_2O_5 / SiO_2



be linear and show no discontinuity. The SiO_2/MoO_3 system was used as a test case.

A series of mixtures containing silica from 0 - 100% molar were prepared, pelleted, and reacted by the standard procedure at 700° and then 0.003 moles were diluted to 1.500g. with MgO in each case. Limit absorption measurements were made at 270, 300, 330, 370 and 400mμ and were scaled relative to reflectance readings taken at 500mμ at which neither component absorbs. An average of the results from four surfaces was taken in each case.

The plots of absorption against composition are shown at several wavelengths in Fig. 6; included are the results obtained for two mixtures which were not heated. In each case linear behaviour of absorption from 0 - 100% silica is observed and the points for the unreacted mixtures also fall on the line.

Reaction between Zinc Oxide and Molybdenum Trioxide:

Solid state reaction between ZnO and MoO_3 was first reported by Carli (1925) who found that an equimolar mixture showed exothermic effects at 270° and 700°. Zelikman (1956), however, noted that the primary and repeated heating curves are identical, but by x-ray methods and by an extraction method in which heated mixtures were leached with aq. NH_4OH, he showed that reaction does take place and that the product $ZnMoO_4$ is formed .

A series of reacted mixtures, varying from 0 - 100% molar ZnO were prepared; those between 50 - 100% molar ZnO were white in colour suggesting the absence of the pale yellow MoO_3 in those reacted mixtures: Zelikman, however, reported that $ZnMoO_4$ is light rose in colour.

Reflectance measurements were taken at 330, 340, 350, 360, 370, 380, 400 and 420mμ at a dilution of 0.00300 moles in 1,500g. of MgO mixture. Direct plots/

FIG 7

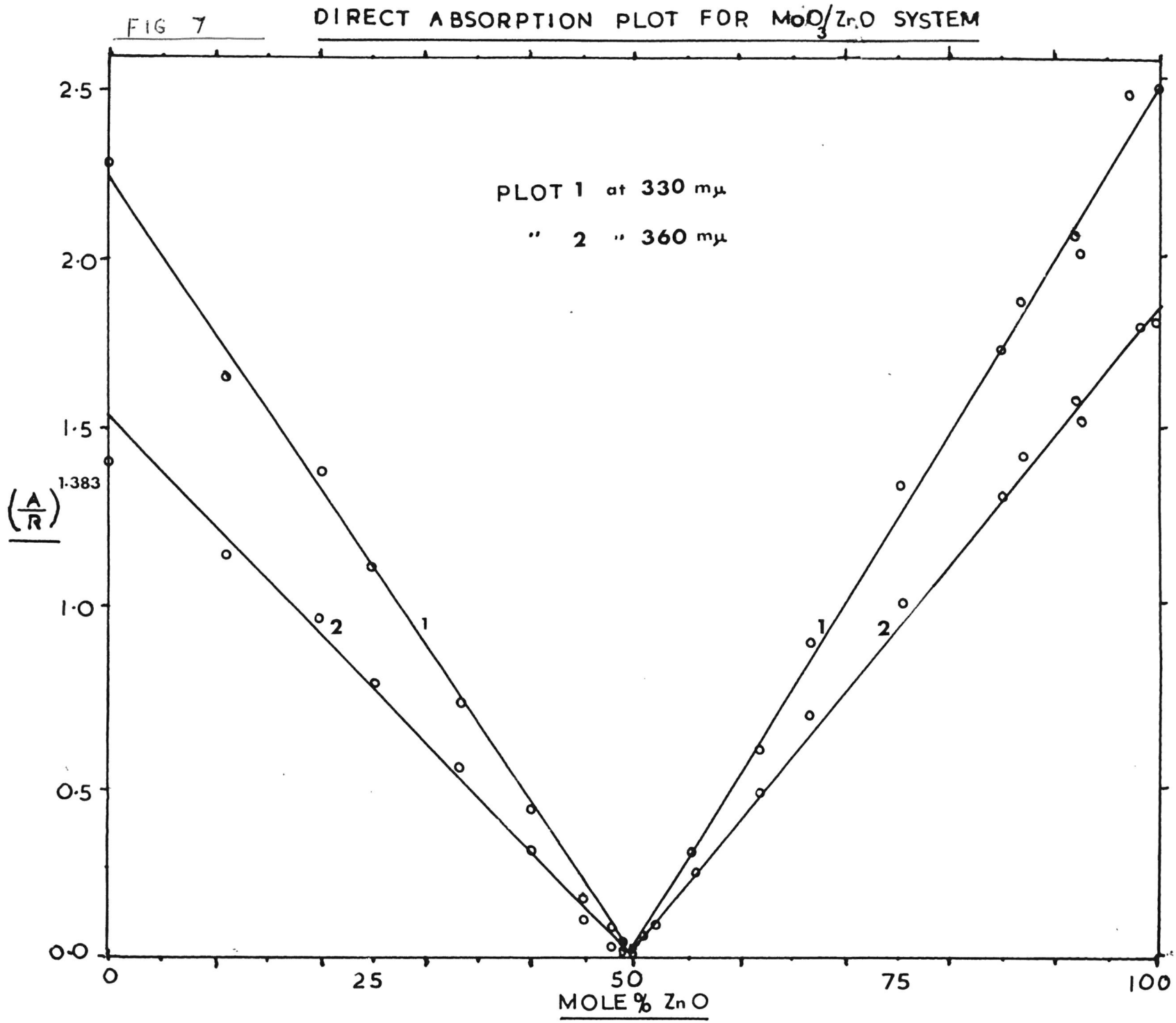

DIRECT ABSORPTION PLOT FOR MoO3/ZnO SYSTEM
PLOT 1 at 330 mμ
" 2 " 360 mμ
(A/R)
1.383
2·5
2·0
1·5
1·0
0·5
0·0
0
25
50
75
100
MOLE % ZnO
1
2

FIGURE 8

JOB'S PLOT FOR MoO_3/ZnO

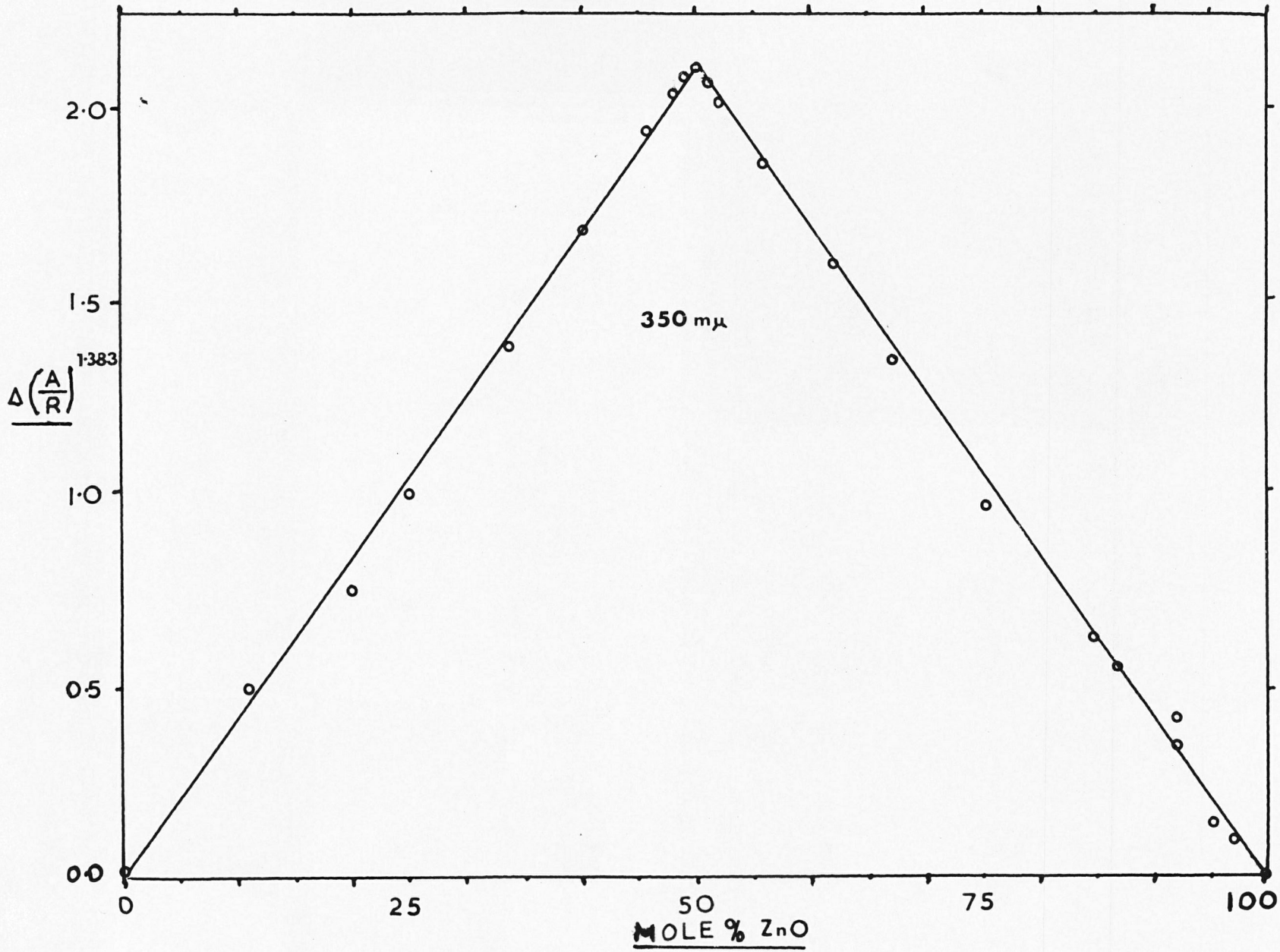
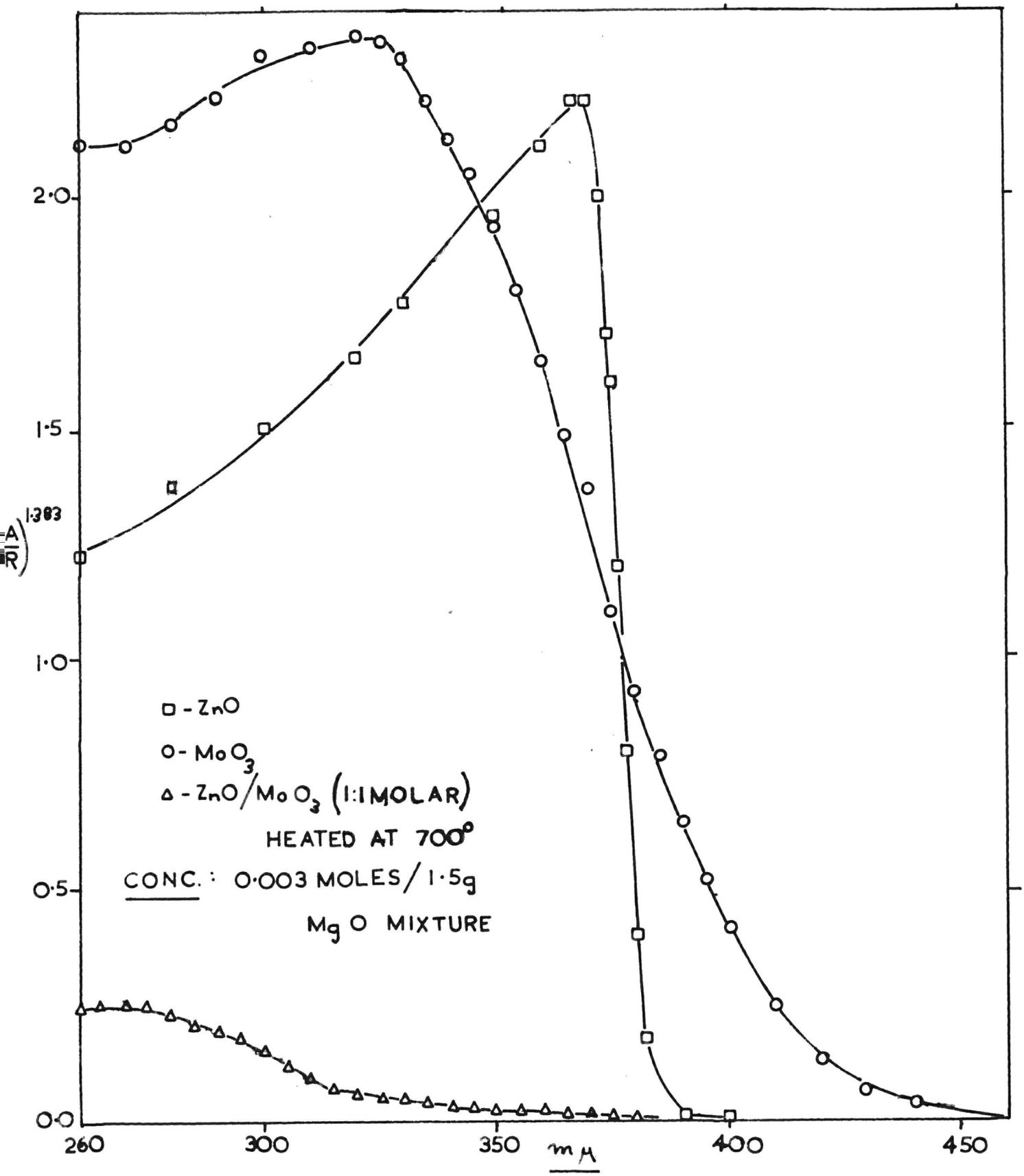


FIGURE 9 SPECTRUM OF ZnO, MoO_3, AND $ZnMoO_4$



plots of absorption against composition are shown at 330 mμ and 370 mμ in Fig. 7, and a plot by Job's mthod at 350 mμ in Fig. 8. The composition of the product was obtained at the intercept of the best straight lines through the points: the results at all wavelengths gave the composition of the product as 50.0 ± 0.2% ZnO, corresponding to a ZnO: MoO_3 ratio of 1.00 ± 0.01: 1, and therefore the normal molybdate. The absorption spectra of ZnO, MoO_3 and Zn MoO_4 were measured and are shown in Fig. 9. The Zn MoO_4 absorbs only in the ultraviolet and it is concluded that the light rose colour observed by Zelikman was due to impurities.

The x-ray powder patterns of a selection of the reacted mixtures, particularly those around 50% molar ZnO, were obtained. The quality of the photographs in the 50% region was poor, the background being diffuse and the lines being relatively broad. The phases observed are shown in Table 19.

Table 19.

Phases in the ZnO - MoO_3 System.

% ZnO	Phase
0.00	MoO_3
24.50	MoO_3 + R.P.
40.10	"
45.63	R.P.
47.94	"
49.97	"
52.00	"
56.61	"
61.97	R.P. + ZnO
66.67	"
100.00	ZnO.

The d spacings of the lines present in the MoO_3 and ZnO photographs agreed with previous publication (Swanson, 1953b and 1953c).

The composition of the reaction product, R.P., from this study cannot be determined accurately, being somewhere in the range 43 - 57% molar ZnO, corresponding to a $ZnO:MoO_3$ ratio of 0·75 - 1.30. The d spacings of the lines present in the Zn MoO_4 photograph are shown in Table 20; since the background was particularly bad, it was difficult to estimate the relative intensities of the lines visually and the figures quoted are only approximate.

Table 20.

d Spacings of Zn MoO_4.

d spacing (Å)	Intensity
3·52	50
3·30	100
2·95	20
2·64	50
2·04	20
1·94	20
1·600	20
1·505	20

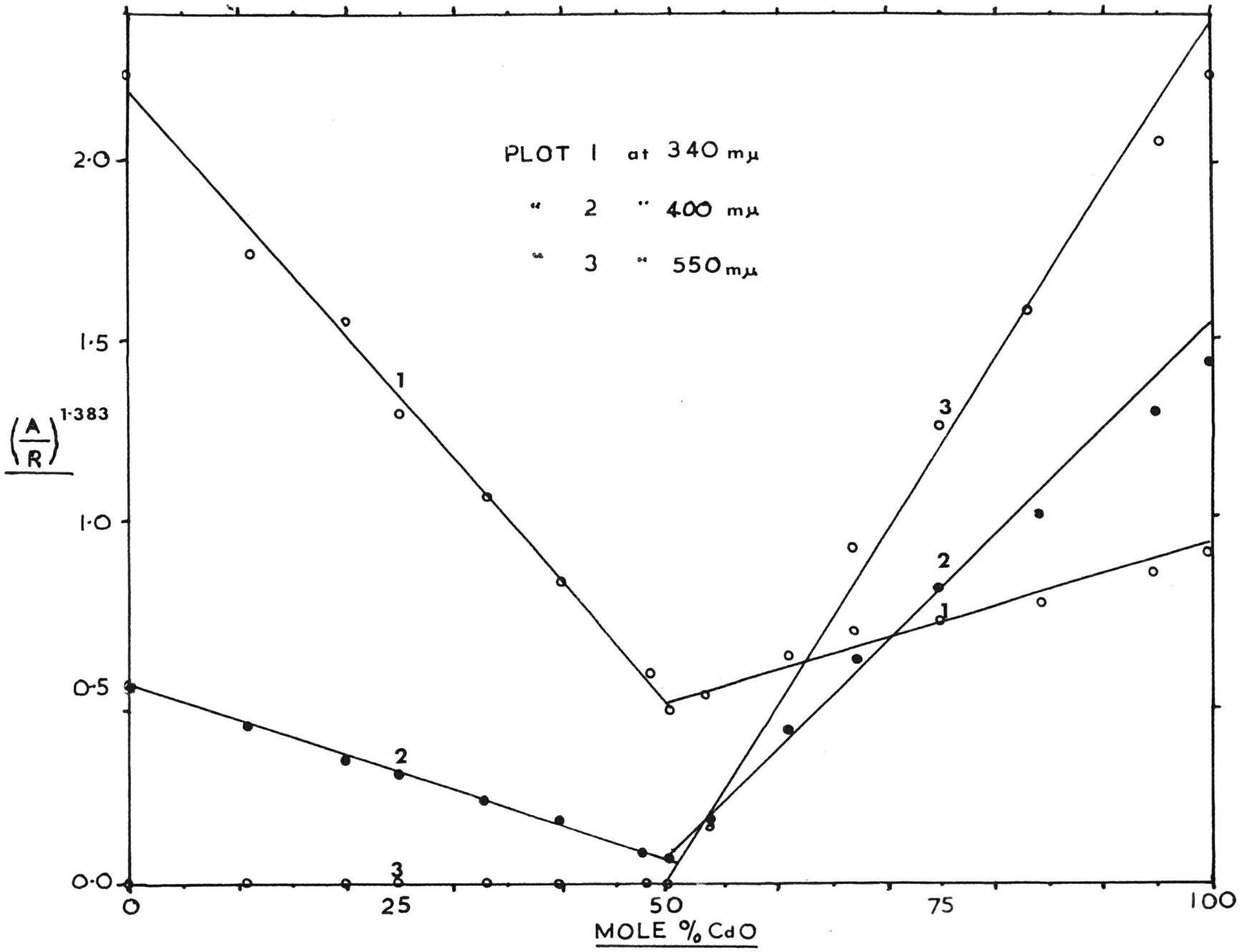
The reflectance procedure was therefore found to work exceedingly well for this system, only one product of molar ratio $ZnO:MoO_3$ of 0·99 - 1·01 being located. The formation of the Zn MoO_4 was confirmed by the x-ray method, which, in this case, proved to be less sensitive to a small excess of a reactant.

Reaction between Cadmium Oxide and Molybdenum Trioxide:

Carli (1925) observed an exothermic effect on heating CdO with MoO_3 but no experimental evidence has been presented for the nature of the product in this solid state reaction, though Jander (1930) showed, by analysis, that a layer of Cd MoO4 is formed between pressed tablets of CdO and Zn MoO_4 on heating. The reaction /

FIGURE 10

ABSORPTION PLOTS FOR MoO_3/CdO



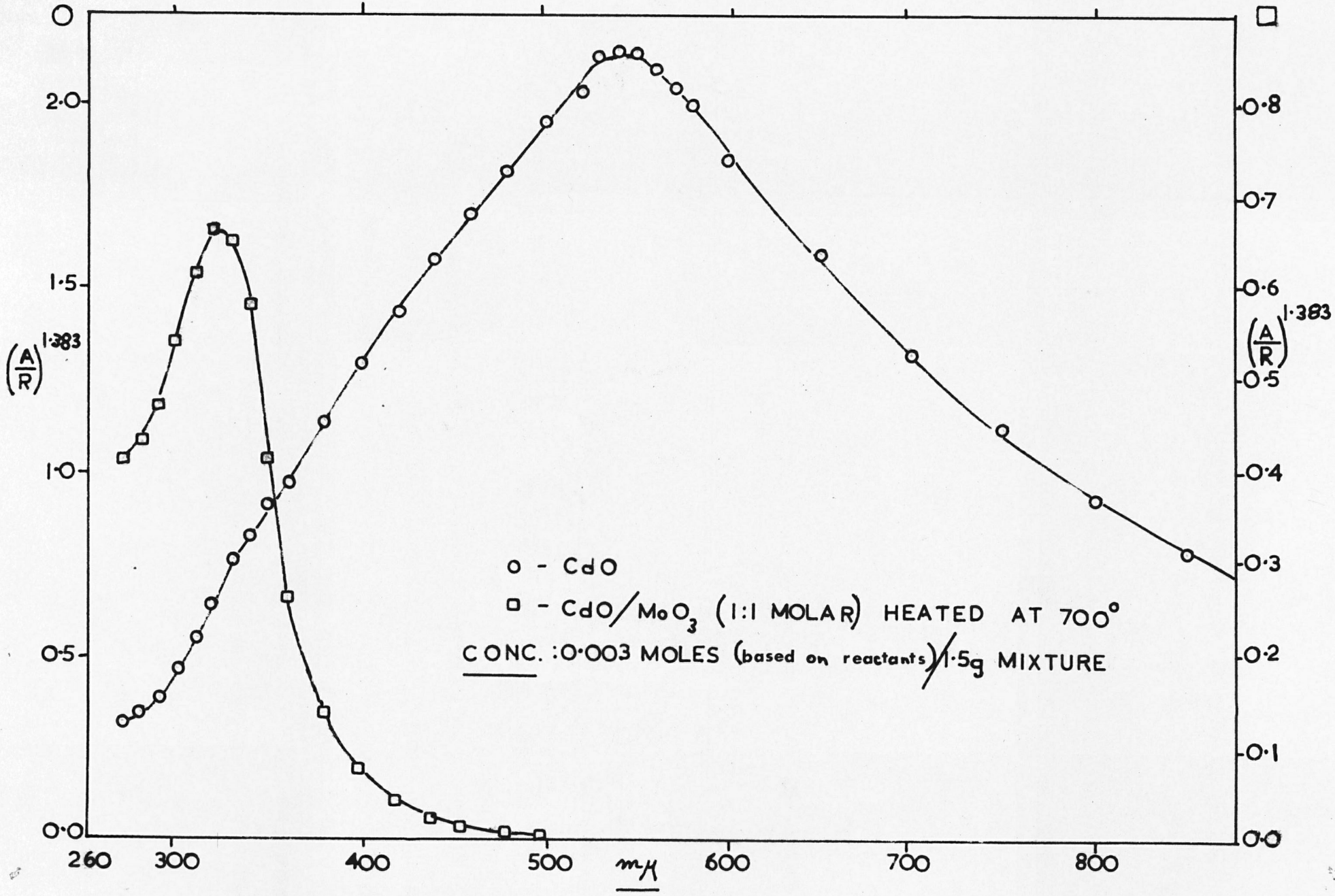
reaction between cadmium salts and sodium molybdate in solution was studied by Saxena (1960) who showed, by amperometric and conductometric methods, that only $CdMoO_4$ is formed. More definite evidence for the formation of the normal molybdate in the solid state reaction between CdO and MoO_3 is reported here.

The CdO, after heating to 700° was brownish-purple in colour, this being slightly different in shade to the unheated material, but since no appreciable weight loss was observed it was concluded that no decomposition had occurred (Schroder (1941) reports that CdO is stable until 800°). All mixtures with MoO_3 were brownish-purple in colour but, after reaction, only the mixtures containing more than 50% CdO retained this colour, the 0-50% CdO mixtures being light yellow.

Reflectance measurements were taken over a wide wavelength range at 600, 550, 500, 400, 380, 360, 350, 340 and 330 mμ to observe the visible CdO absorption and the ultraviolet MoO_3 absorption. In each case an average of the results from five surfaces was taken, but since the CdO absorbs throughout the wavelength range studied, it was not possible to scale the absorption readings relative to a reflectance measured in the region of no absorption. Typical direct absorption/concentration plots at 340, 400 and 550 mμ are shown in Fig.10. At 550 mμ only the CdO absorbs and this is one of the few cases in which the composition of the product can be deduced directly from the measured absorption of a reacted mixture containing one of the reactants, here CdO, in excess. The scatter of points from the best straight lines was somewhat greater than for the ZnO system, but this is to be expected since the measured absorptions were not corrected for reflectances differing from 100% in the region of no absorption. The intersections of the lines were in the range 49·7 - 50·7% CdO

for/

FIGURE 11 SPECTRUM OF CdO AND $CdMoO_4$



for the nine wavelengths measured corresponding to a molar ratio $CdO:MoO_3$ of 0·99 - 1.03, showing that Cd MoO_4 is formed. The spectra of CdO and Cd MoO_4 are shown in Fig. 11.

The x-ray powder photographs of a number of reacted mixtures were studied and the phases observed are shown in Table 21.

Table 21.

Phases in CdO - MoO_3 System

% CdO	Phase
0·00	MoO_3
33·32	MoO_3 + R.P.
39·97	"
43·00	R.P.
48·05	"
50·00	"
53·73	"
56·80	"
61·16	R.P. + CdO
66·74	"
100.00	CdO

The lines due to the CdO, accorded with previous publication (Swanson and Fujat, 1953a). The reaction product, R.P., lines in the possible composition range 43 - 57% CdO, corresponding to a molar ratio of $CdO:MoO_3$ of 0·75 - 1·30, confirming the formation of Cd MoO_4 in this reaction. The d spacings of Cd MoO_4 measured, agreed with those previously published (Swanson 1956) as is shown in Table 22.

Table 22.

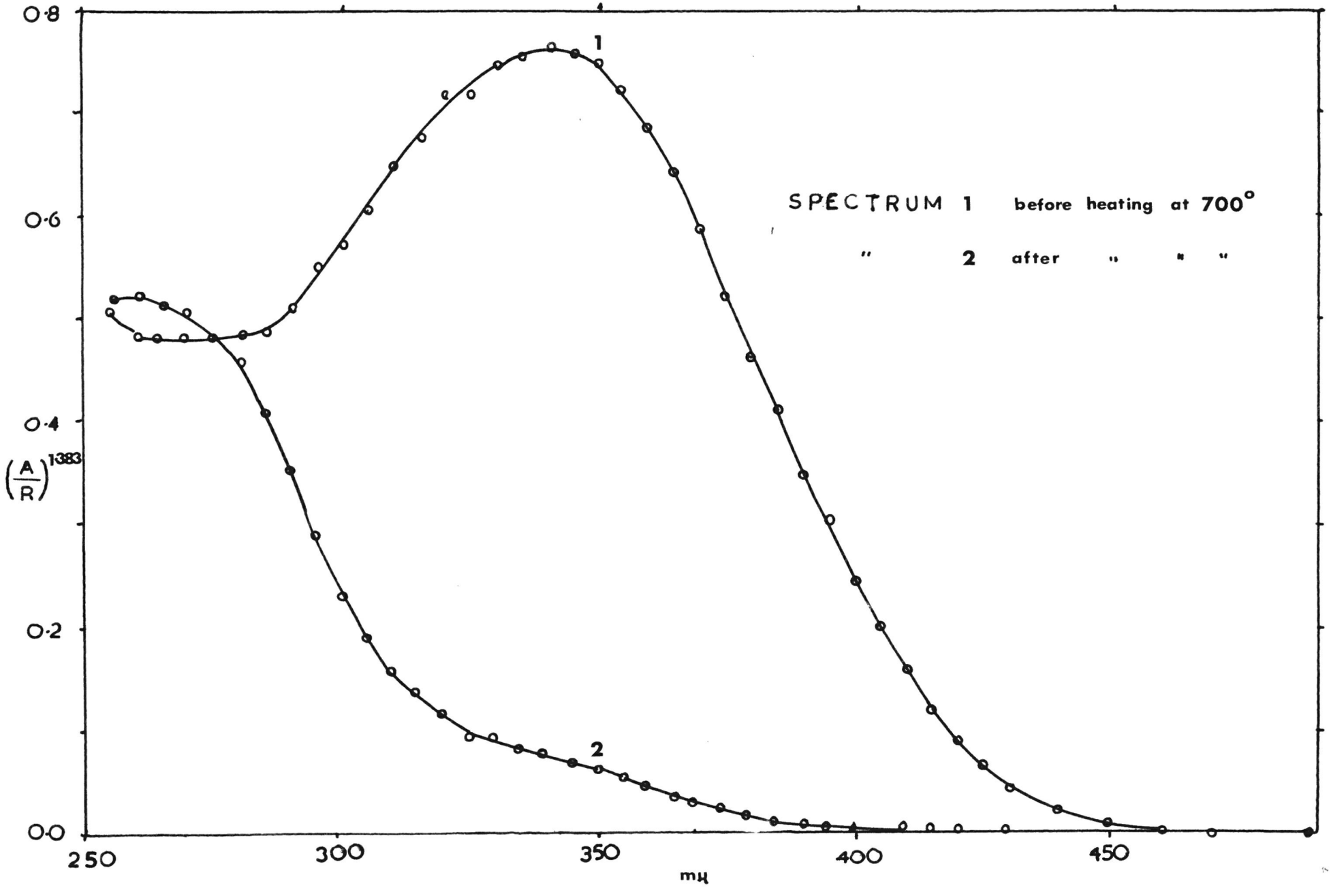
d Spacings of Cd MoO_4.

d Å	
This Work	Swanson
3·01	3·054
2·76	2·798
2·54	2·576
-	2·259
-	2·220
1·880	1·896
1·814	1·823
1·644	1·661
1·553	1·565
1·517	1·528
-	1·400
1.275	1·289
1·218	(1·230 (1·228
1·179	1·188
1·162	1·171
1·146	1·153
1·101	1·111
-	1·0703
1·060	1·0659
1·013	1·0183
+ 11 lines to 0·7812	+ 17 lines to 0·7825

The lines agreed in relative intensity as well as position. Good agreement between the reflectance and x-ray methods was again found, both illustrating the formation of Cd MoO_4 in the solid state. The reflectance method was again found to be much more sensitive to a small excess of a reactant so that the composition of the product could be defined more accurately.

FIGURE 12

SPECTRA OF MoO_3/MgO MIXTURES



Reaction between Magnesium Oxide and Molybdenum Trioxide:

From a study of the heating curve of a mixture of MgO + MoO_3, Carli (1925) concluded that no reaction occurs, whereas Tamman and Westerhold (1925) by a similar study observed an exothermic effect at 425° showing the presence of solid state reaction. This system was studied in the present work to determine if reaction does take place.

A mixture of MgO and MoO_3 (1:1 molar) was prepared and a portion of this, after pelleting, was heated to 700° overnight. The heated mixture was pure white, and this indicated the absence of MoO_3.

The reflectance spectrum of the mixture was found to be appreciably changed by heating as is shown in Fig. 12. The heated mixture is only very weakly absorbing in the 350 - 400 mμ region, showing that MoO_3 is virtually absent, and has an absorption maximum at 260 mμ which is probably due to $MgMoO_4$.

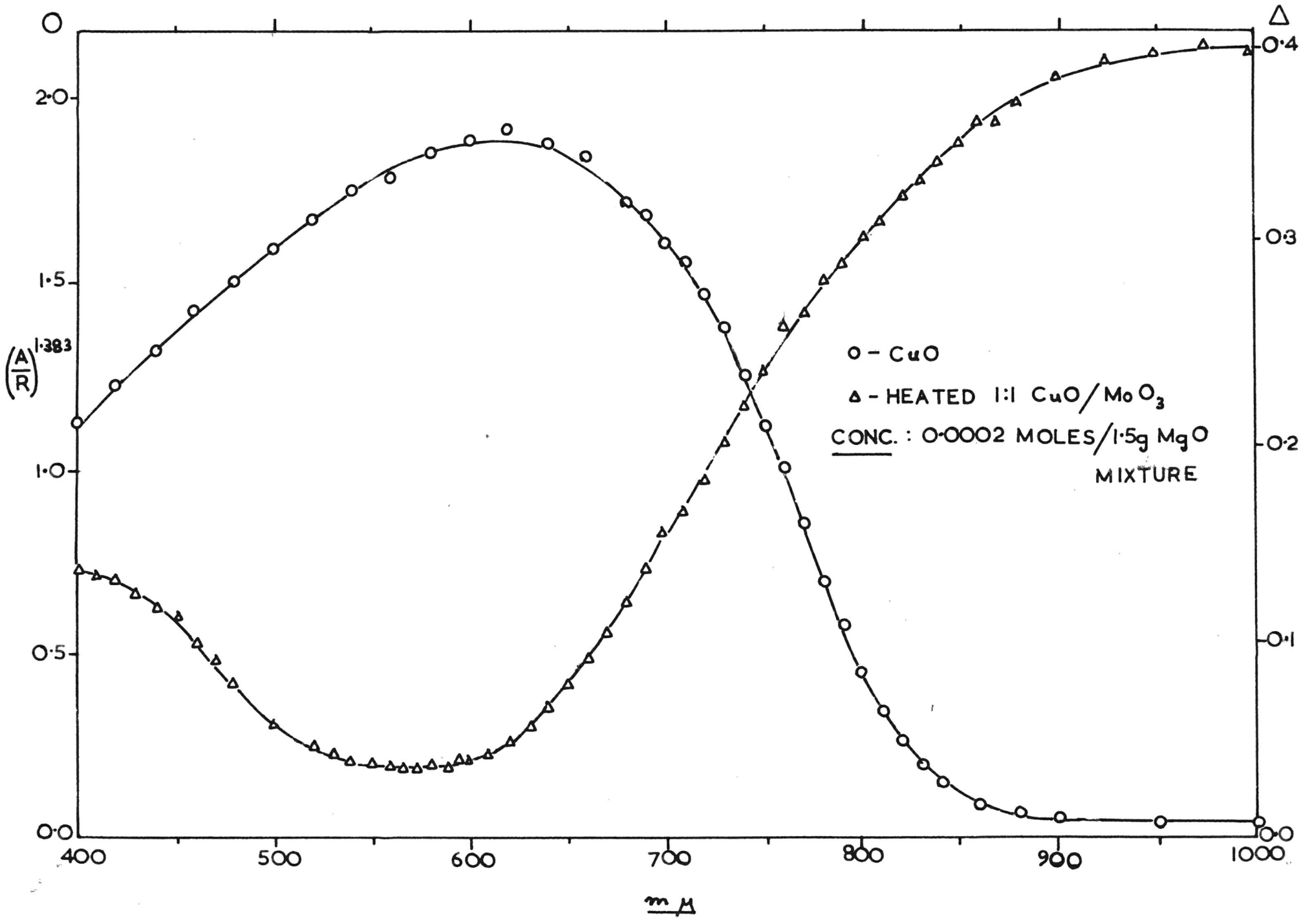
The x-ray powder photograph of the heated mixture showed no lines whatsoever, only a dark background being visible. Although giving no clue to the nature of the product, this does confirm that reaction has occurred.

Reaction between Copper Oxide and Molybdenum Trioxide:

Tamman and Westerhold (1925), from a comparison of the primary and secondary heating curves of an equimolar mixture of CuO and MoO_3 established that solid state reaction occurs. Zelikman (1944, 1956) by x-ray and chemical extraction methods showed that $CuMoO_4$ is formed but noted that in his heating curves the exothermic effects are not very conspicuous due to the low heat of formation of the molybdate from the oxides.

The preheated CuO was black in colour and its spectrum is shown in Fig. 13. Included in this figure is the spectrum of a CuO/MoO_3 mixture (1:1 Molar /

FIGURE 13 SPECTRUM OF CuO AND $\dot{C}uMo\bar{O}_4$



(1:1 molar) which had been heated overnight at 700°, showing that reaction takes place on heating. Continued heating of the 1:1 mixture, however, brought about further spectral changes, not in the positions of the new absorption bands, but in their intensities as is shown in Table 23.

Table 23.

Absorption, $(\frac{A}{B})^{1\cdot383}$ of Product

Time (Hrs.)	575mμ	950mμ
0	1·04	0·02
15	0·02	0·40
24	0·04	0·38
80	0·02	0·29
105	0·03	0·29
130	0·02	0·20

The low absorption at 575mμ after the first heating period suggests that the CuO has been completely reacted after this time. The absorption at 950mμ is seen to increase after the first heating period, due to the formation of the reaction product, but then decrease steadily on continued heating. For the same heating period the absorption at 950mμ was less when the reaction was carried out at higher temperates (eg. after 24 hours at 750° it was 0·24) and greater at lower temperatures (eg. after 24 hours at 550° it was 0·51). Since the reaction was virtually complete after 15 hours these variable absorptions would appear to be due to differences in the crystallinity of the product; evidence for this was obtained in the x-ray study.

A series of mixtures from 0 - 100 molar % CuO, all black in colour were reacted under the standard conditions. The 0 - 50% CuO reacted mixtures were /

FIGURE 14

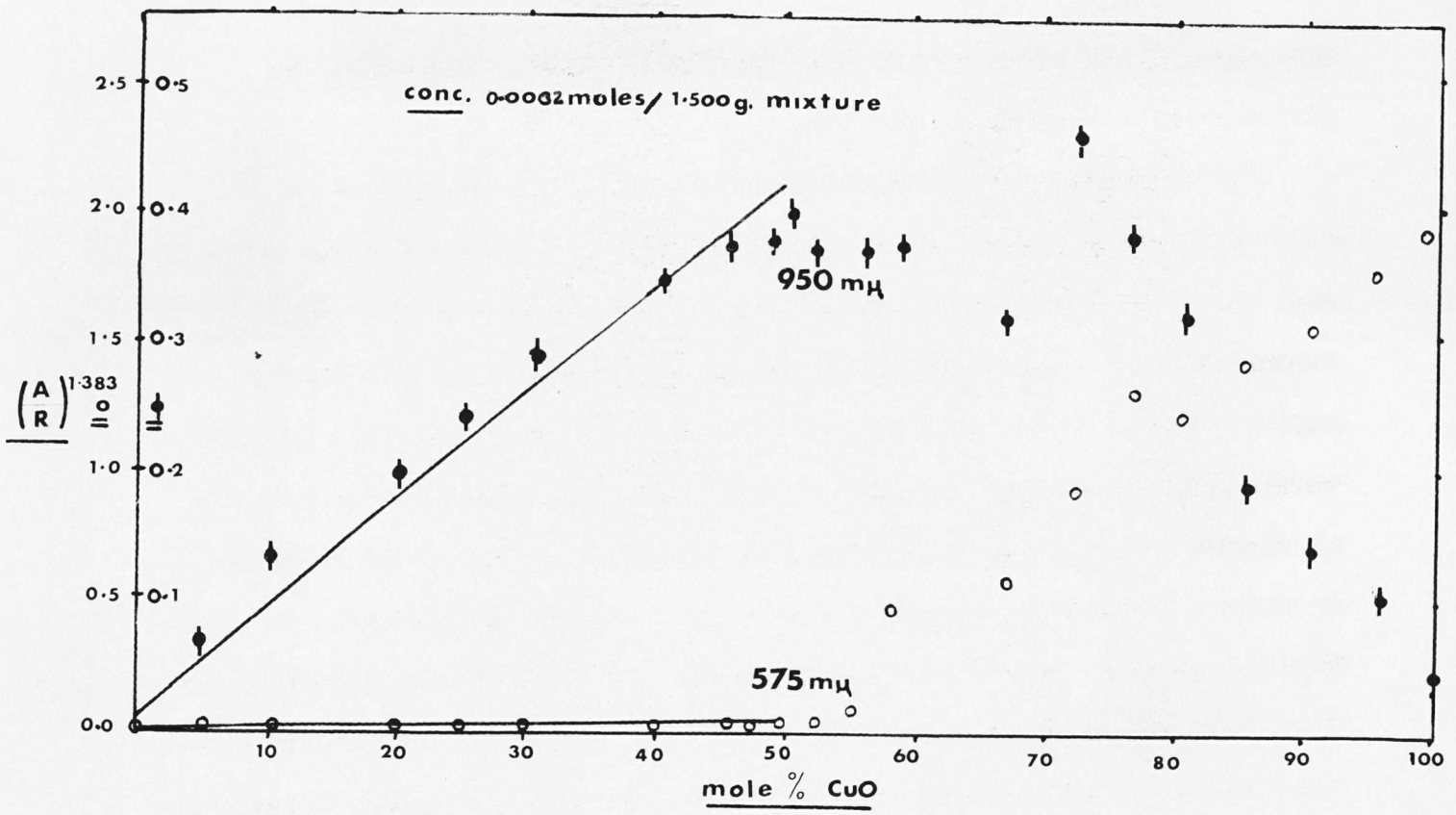
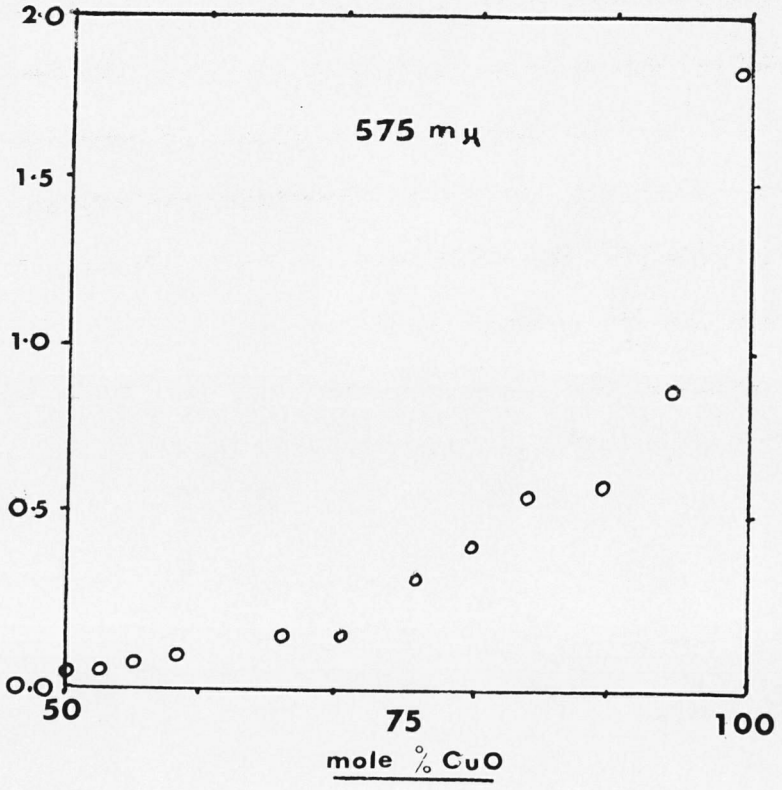


FIGURE 15



were green in colour and those from 50-100% CuO black, suggesting the formation of a compound at 50% CuO.

The reflectance measurements were taken at 575mμ and 950mμ at a dilution of 0·0002 moles per 1·500g MgO mixture and the results are shown in Fig. 14. For 0-50% CuO reacted mixtures linear behaviour of absorption with composition was observed at both wavelengths but not in the 50-100% CuO region where a regular variation of absorption was not observed. At both wavelengths, however, a break in the plot around 50% CuO is evident. The absorptions of mixtures containing more than 50% CuO were found to be decreased by continued heating, particularly at 575mμ where the CuO absorbs strongly. Mixtures which contained only a small excess of CuO were more rapidly decreased than those containing a large excess. Fig. 15, in which the results obtained for a series of mixtures reacted at 750° for 24 hours are shown, illustrates this. On continued heating of the 75-100% CuO mixtures at 750° the absorptions at 575mμ did not become constant in four days.

An x-ray study of the reacted mixtures showed that only one product $CuMoO_4$ is formed in this system, whether reaction was carried out at low or high temperature, though the temperature at which the reaction had been carried out did, however, affect the quality of the powder photograph. For the product formed at 500-600° the background was very intense and only a few lines were observed, but for the product formed at 700-750° the quality was greatly improved. For example, the lines observed after heating a 1:1 mixture for 24 hours at 600° and at 750° are shown in Table 24.

Table 24.

d spacings of $CuMoO_4$.

d spacing (Å)		Intensity
600°	750°	
3·82	3·77	100
3·32	3·25	100
3·07	3·05	50
2·75	2·75	50
	2·24	20
1·71	1·71	30
1·585	1·575	30
	1·515	20
	1·435	20
	1·333	20
	1·256	20
	1·116	20
	1·070	20
	1·043	20
	1·007	20
	+ 12 lines to 0·7895	⩽ 20

The improvement in the quality of the photograph on continued heating suggests an improvement in the crystallinity of the material.

Since only the 1:1 molar compound is formed the changes in the spectrum of mixtures containing excess CuO may also be due to the improvement of the crystallinity of the CuO. Since the spectrum of pure CuO does not change appreciably on continued heating at these temperatures, the changes observed in the mixtures would appear to be assisted by the product. Evidence for this is the relatively rapid changes observed for mixtures containing a large product to CuO ratio, compared with the mixtures containing a low product to CuO ratio.

The /

FIGURE 16

SPECTRUM OF NiO AND $NiMoO_4$

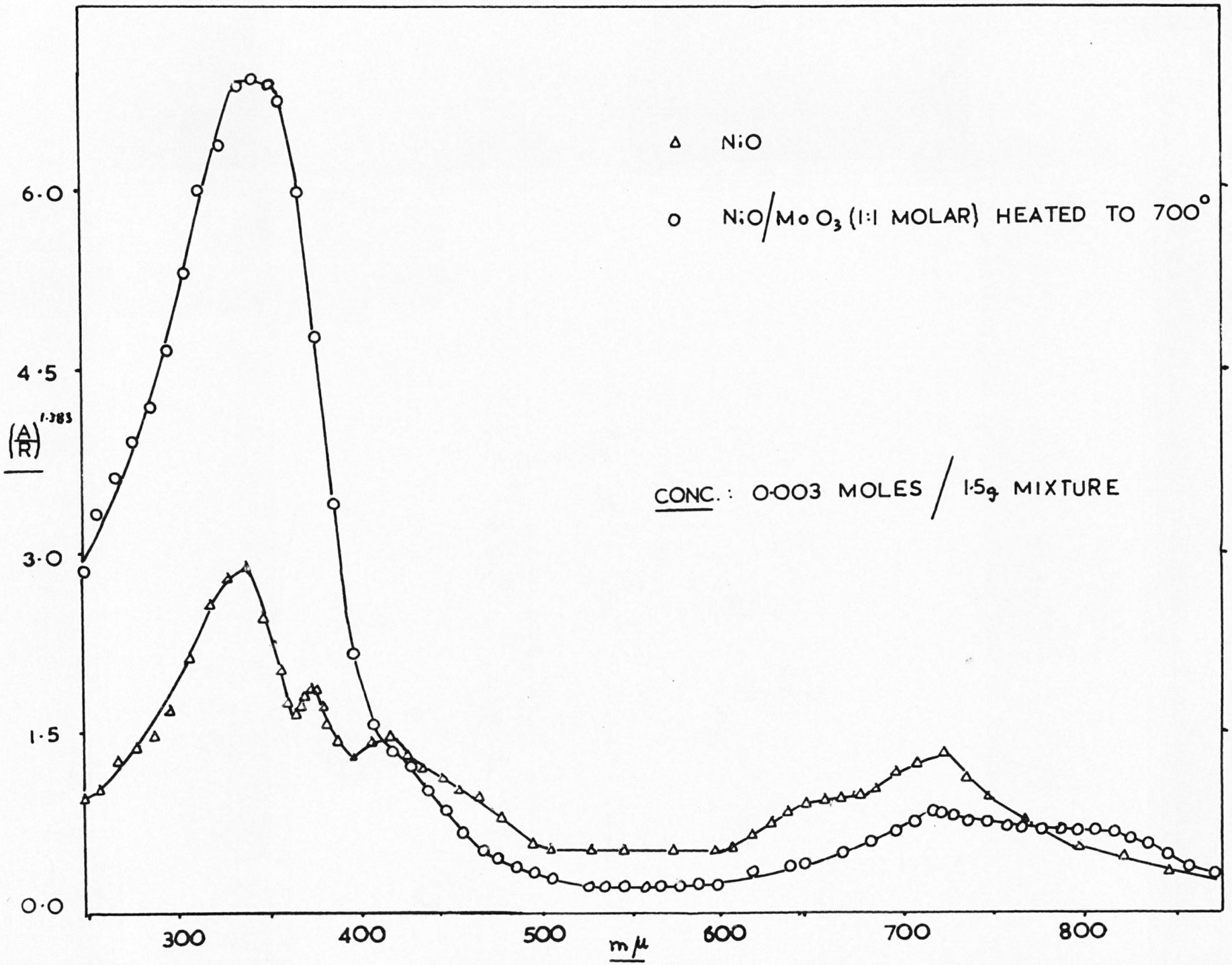
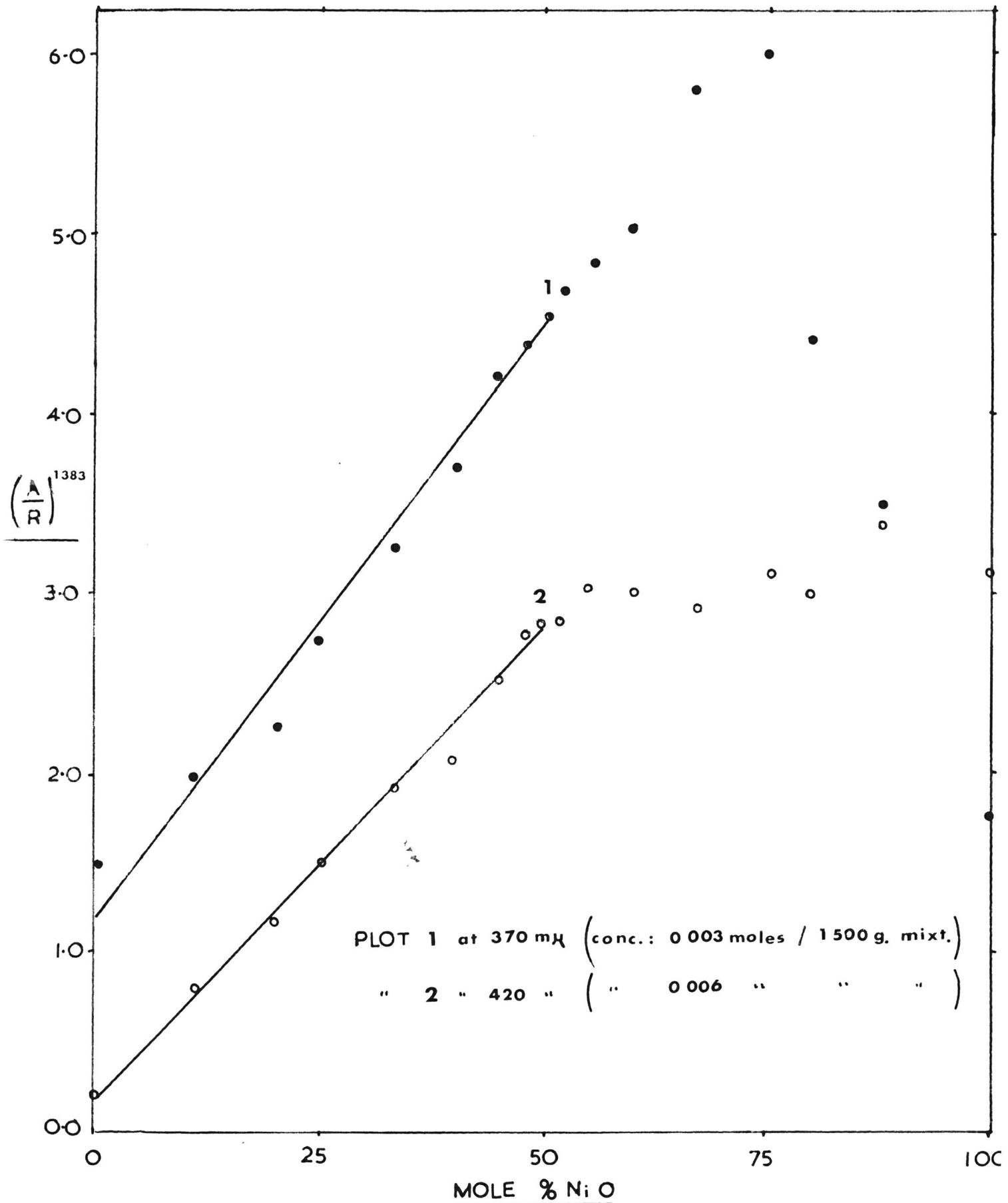


FIGURE 17 ABSORPTION PLOTS FOR MoO_3/NiO



The spectrum of pure CuO, however, changed on heating it to higher temperatures and this study is reported in Section III.

Reaction between Nickel Oxide and Molybdenum Trioxide:

Carli (1925) established from heating curve studies that solid state reaction between NiO and MoO_3 commences at 495°. Silvent and Trambouze (1958), studied this reaction in detail using x-ray and chemical extraction methods, and showed that Ni MoO_4 is formed.

Green stoichiometric nickel oxide was prepared by heating the nitrate to 950° (Chufarov et al.,1950). A pelleted mixture of NiO and MoO_3 (1:1 molar) was heated to 700° and its spectrum, as well as that of the pure NiO, is shown in Fig. 16. Though the spectra are similar the differences are sufficient to establish that reaction has occurred. The x-ray powder photograph of the heated mixture confirmed reaction.

Mixtures of NiO and MoO_3 were reacted by the standard procedure at 700°. It was not possible to detect a change in colour in this case at 50 molar % metal oxide since both the 1:1 reacted mixture and NiO were green, though of slightly differing shade.

Reflectance measurements were made at 350, 370, 390, 420, 540, and 720mμ after reaction. Typical results are shown in Fig. 17 from which it is seen that the reaction product could not be consistently located at 50% NiO or any other composition. Linear behaviour of absorption with composition was however always observed in the 0-50% NiO region but not in the 50-100% region.

The x-ray powder photographs of reacted mixtures showed that only one product, of approximate composition 50% molar NiO was formed, corresponding to Ni MoO_4. The d spacings of the Ni MoO_4 observed in this work are compared with previous publications in Table 25.

Table 25.

d spacings of $NiMoO_4$.

d spacing (Å)			Intensity
Brenner	Anton	This Work	(This Work)
6·12		6·25	100
3·80		3·77	100
3·48		3·48	100
		3·27	40
3·07	3·11	3·10	100
2·73	2·75	2·72	100
2·31		2·31	20
2·19	2·20	2·13	10
2·06	2·07	2·06	100
		1·96	10
1·91		1·91	15
		1·84	10
1·71	1·72	1·71	10
1·63		1·625	20
1·60		1·582	20
1·50		1·500	20
1·46		1·438	20
		1·400	10
		+ 16 lines	20

The molybdate studied by Brenner (1955) was prepared by reacting the oxides at 500°, and that studied by Anton(X-ray powder data file)was a corrosion product of a Ni/Mo alloy. In this work more lines were observed than in previous work, the additional ones generally being of low intensity, and it is suggested that the reason for this is that a more crystalline product was studied.

Since only one product is formed in this system the irregularity of the absorption for reacted mixtures containing greater that 50% NiO might be due to changes in the spectrum of $NiMoO_4$ or NiO when in admixture.

FIGURE 18

SPECTRUM OF CoO AND $CoMoO_4$

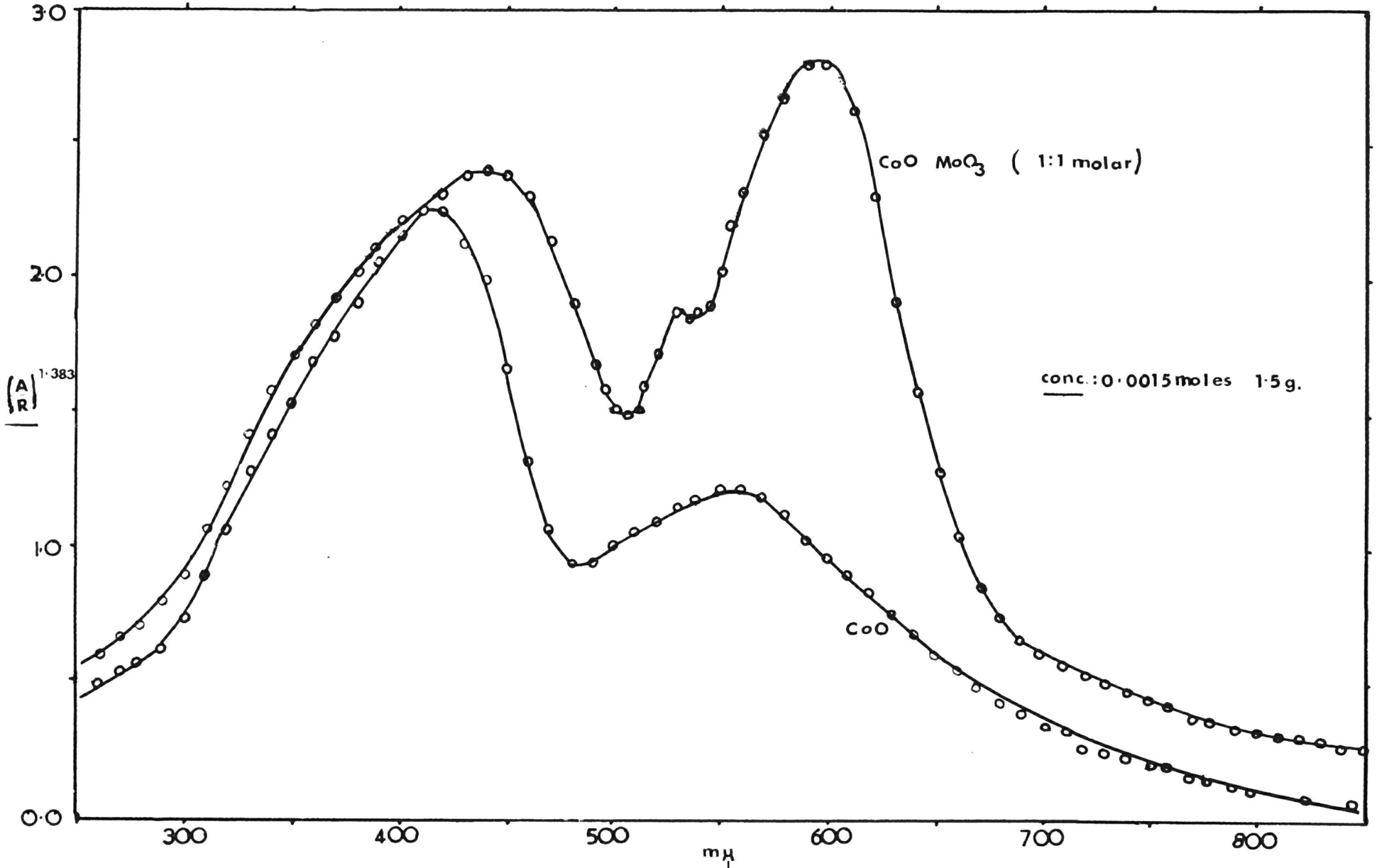
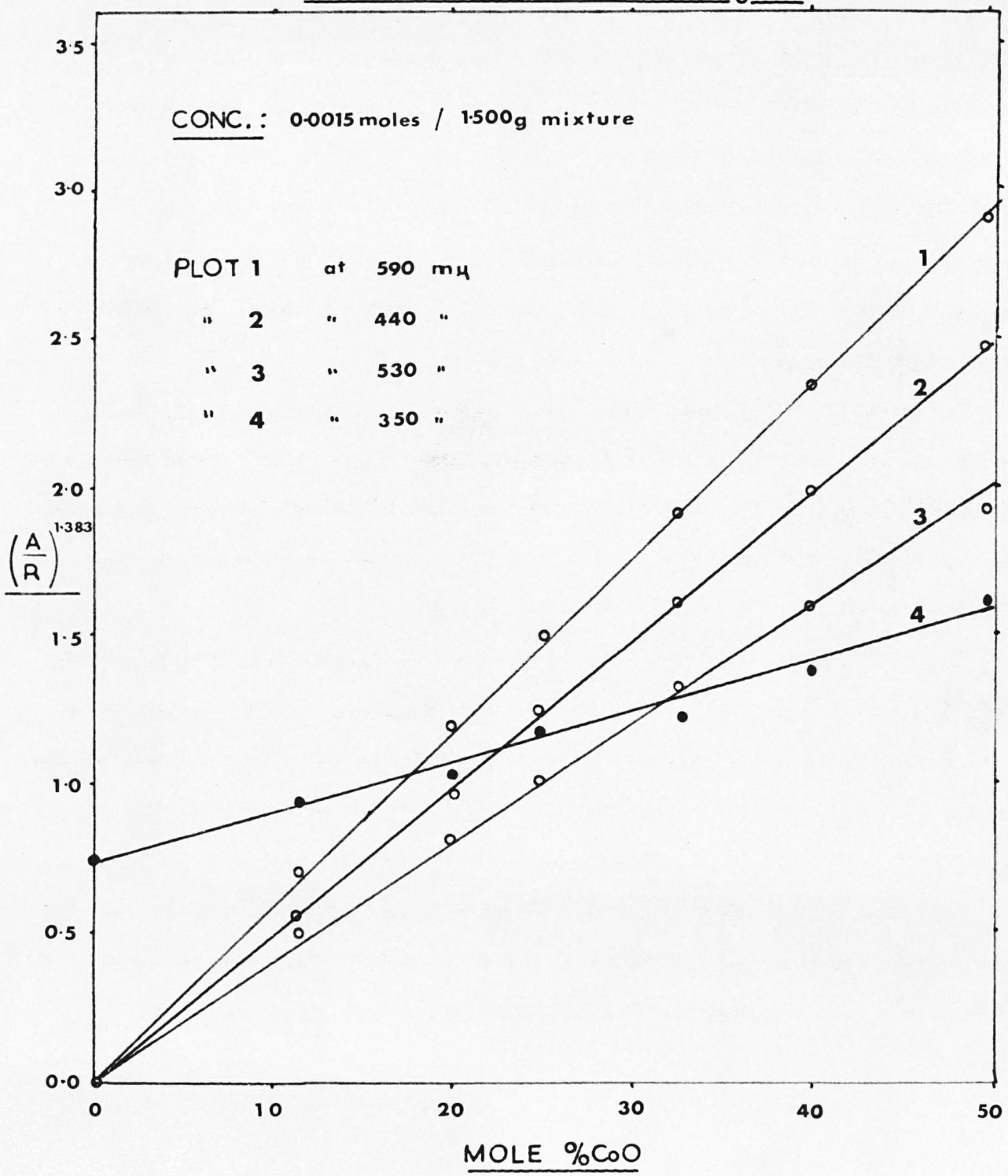


FIGURE 19

ABSORPTION PLOTS FOR MoO_3/CoO



Reaction between Cobalt Monoxide and Molybdenum Trioxide:

Carli (1925) showed that CoO reacts with MoO_3 on heating but no evidence has been presented for the nature of the product.

Cobalt oxide was prepared by heating the carbonate to 950° in a stream of nitrogen to avoid the formation of Co_3O_4 (Chufarov et al., 1950). The product was analysed electrolytically for cobalt at a current of 1 amp. at 3 V. for 2 hours (Williams, 1958) and the percentage found (78·4; 78·5) agreed very well with the expected of 78·61% Co in CoO. The purity of the oxide was confirmed by its x-ray powder photograph, lines due to Co_3O_4 being absent. To avoid the formation of Co_3O_4, the stable oxide at 700°, the mixtures with MoO_3 were heated in a stream of nitrogen: no changes in weight occurred after heating the mixtures.

The spectrum of an equimolar mixture heated to 700° is shown in Fig. 18; included is the spectrum of pure CoO showing that reaction had taken place. For this system, only mixtures containing from 0-50% CoO were studied and after the reaction the pelleted mixtures were lilac, but this was only a surface effect as on grinding green powders were obtained.

The reflectances of the reacted mixtures were measured at 350, 440, 530, 590 and 850mμ and typical results are shown in Fig. 19. Within experimental error linear variation of absorption with composition was observed, showing the absence of a compound of a composition within the range 0-50% CoO, but not of course showing the formation of the normal molybdate.

The x-ray powder photographs of the reacted mixtures showed that only two phases were present. At 50% CoO all the main lines of MoO_3 and CoO were absent, and for the other reacted mixtures the strongest of the lines observed /

observed in the 50% CoO reacted mixture, as well as those of MoO_3 were present. This, therefore, shows the formation of Co MoO_4, the d spacings of which are shown in Table 26.

Table 26.

d spacings of Co MoO_4.

d spacing (Å)	Intensity
4·50	100
3·52	50
3·15	50
2·70	50
2·34	5
2·22	5
2·07	25
1·93	10
1·735	10
1·62	10
1·515	15
1·420	5

The reflectance method of determining the composition of the product formed in solid state reactions has therefore been shown valid for most of the systems studied. The exceptions were the MoO_3 - transition metal oxide systems: possible reasons for this are presented in the Discussion.

II. C. Systems not Previously Studied.

The reactions in the solid state between MoO_3 and the following oxides: SnO_2, GeO_2, ThO_2, ZrO_2, B_2O_3, have not been previously studied. It has been stated that Al_2O_3 does not react with MoO_3 but since this was based only on the study of heating curves, the unreliability of which has been previously noted /

FIGURE 20

SPECTRUM OF MoO_3/SnO_2

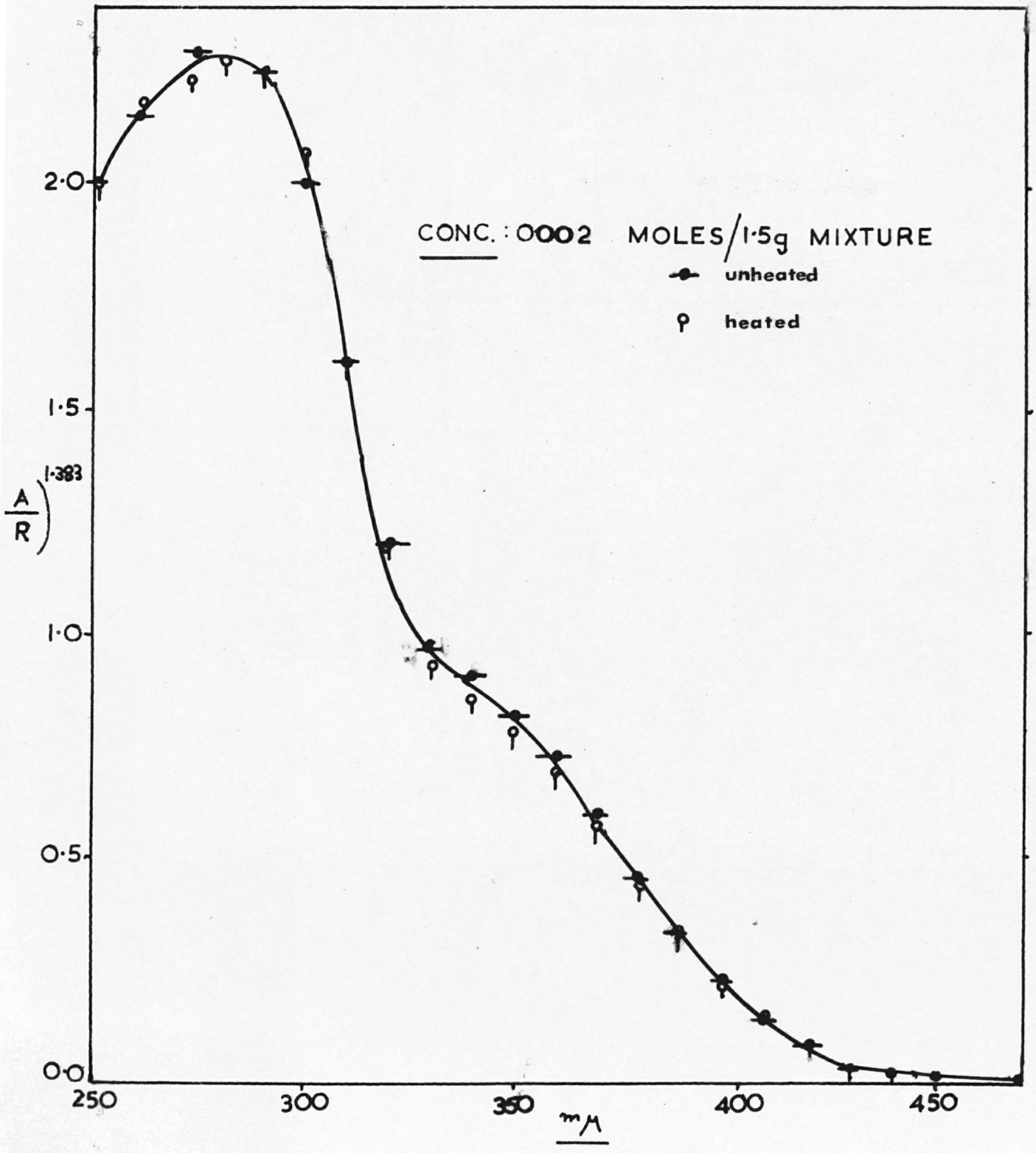
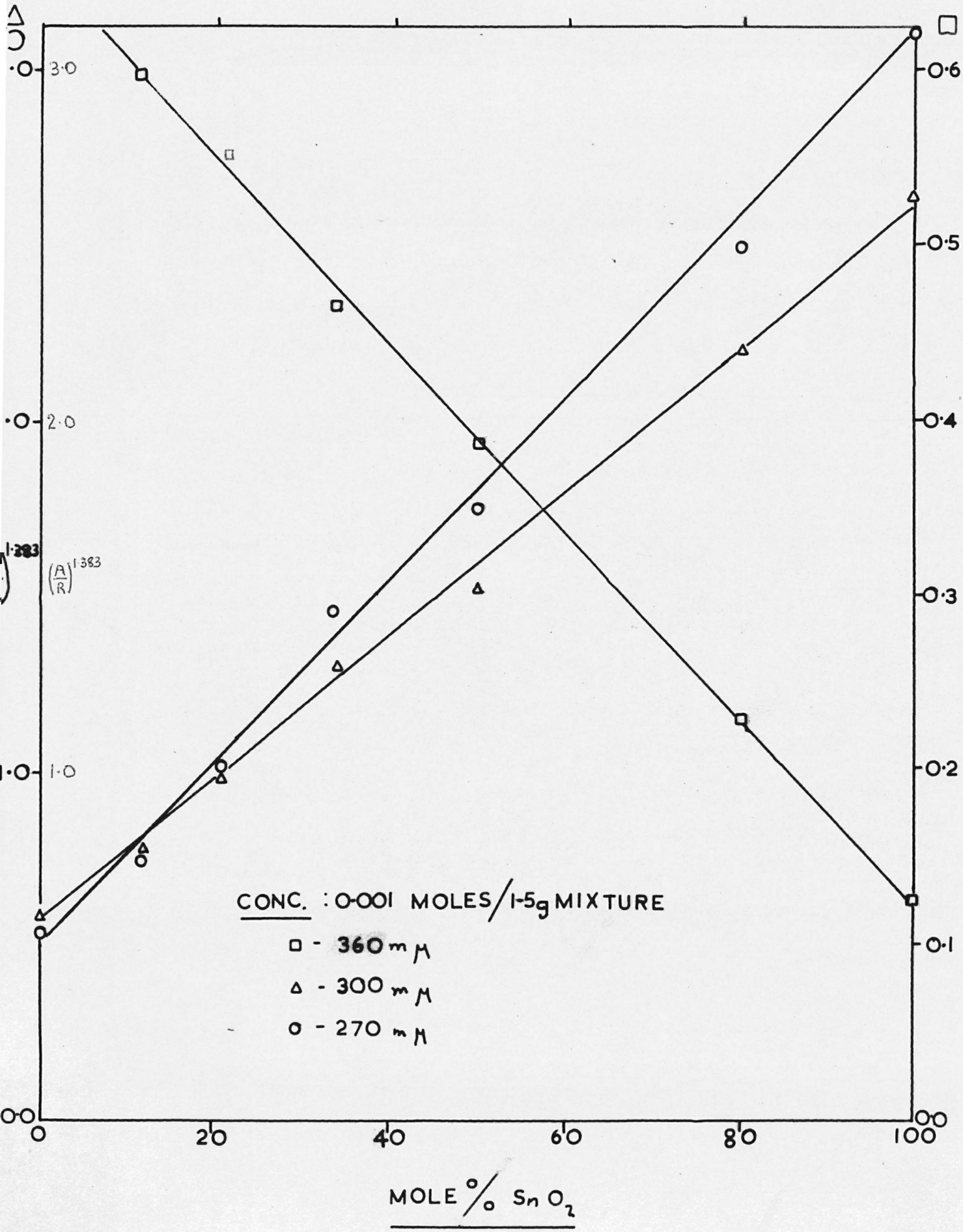


FIGURE 21

ABSORPTION PLOTS FOR SnO_2/MoO_3



noted, this cannot be regarded as conclusive evidence.

In this work these systems were investigated by the reflectance method and by the x-ray method.

Reaction between Stannic Oxide and Molybdenum Trioxide:

No information exists on the reaction between SnO_2 and MoO_3 in the solid state though stannic molybdate has been prepared as a gel from solution (Prakash et al., 1929). The formation of a substance as a gel does not, however, mean that it will necessarily be stable in an anhydrous form, since in the hydrated salts the co-ordinated water stablises the anion from the polarizing power of the cation.

A mixture of SnO_2 and MoO_3 was heated to 700° and the reflectance spectra, before and after heating, shown in Fig. 20, suggest that no reaction occurred. The x-ray photographs of the heated and unheated mixtures were identical, containing only lines due to the reactants, confirming that no reaction had taken place.

A series of reacted mixtures from 0-100% SnO_2 was studied by the reflectance method at 270, 300, 330, 360 and 400mμ to show that linear variation of absorption from 0-100% metal oxide is observed in systems in which no reaction occurs. This has been previously illustrated for the SiO_2-MoO_3 system but in that case only absorption due to MoO_3 was measured, whereas in the present case SnO_2 absorbs strongly in the range 270-360mμ so that absorptions due to both constituents could be measured. Typical plots obtained are shown in Fig. 21, from which it is concluded that the variation of absorption with composition is as expected.

FIGURE 22

SPECTRA OF GeO_2/MoO_3

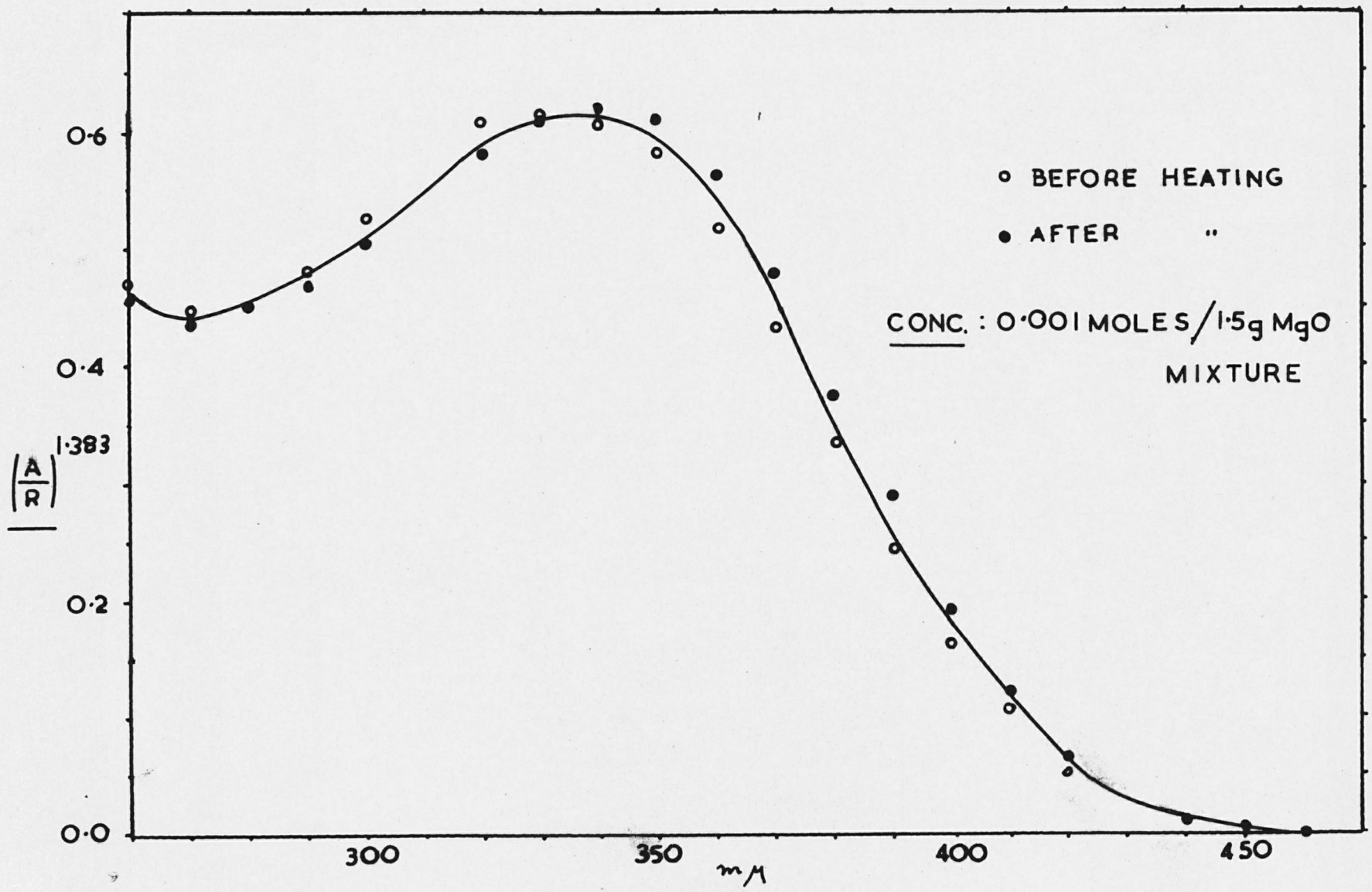
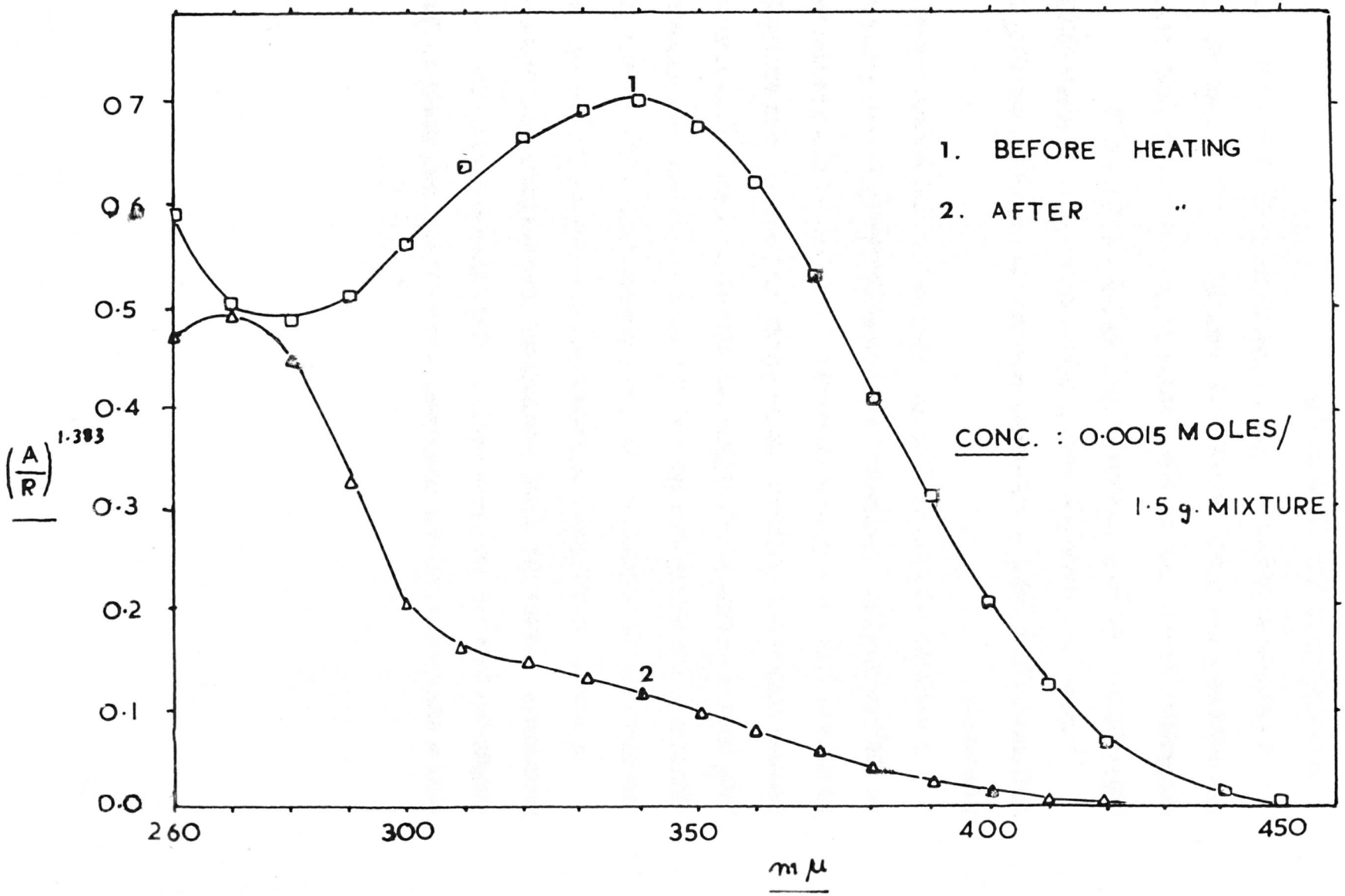


FIGURE 23

SPECTRUM OF MoO_3 / ThO_2



Reaction between Germanium Dioxide and Molybdenum Trioxide:

No information exists on the formation of germanium molybdate either in solution or in the solid state.

A mixture of GeO_2 and MoO_3 was heated to 700° in the usual way. The reflectance spectra before and after heating, shown in Fig. 22, are identical suggesting that no reaction had taken place: the x-ray study confirmed this.

Reaction between Thorium Dioxide and Molybdenum Trioxide:

Thorium molybdate has been prepared as a gel by Prakash (1929) but no information regarding solid state reaction between MoO_3 and ThO_2 has been published.

A pelleted mixture of ThO_2 and MoO_3 (1:2 molar respectively) was heated to 700° overnight. Appreciable swelling of the disc took place and it changed in colour, from pale yellow to white. The reflectance spectra before and after heating were quite different as is shown in Fig. 23: the absorption band of MoO_3 with a maximum around 335mμ was virtually absent after reaction and in addition a new absorption band with a maximum at 270mμ was present. Reaction was confirmed by a study of the x-ray powder photographs of the mixtures.

A series of ThO_2/MoO_3 mixtures were reacted at 700° by the standard procedure. After the first heating all discs, apart from those of the pure reactants, had swollen appreciably. The diameters were measured approximately with a micrometer and the increases after heating are shown in Table 27.

FIGURE 24

ABSORPTION PLOTS FOR MoO_3/ThO_2

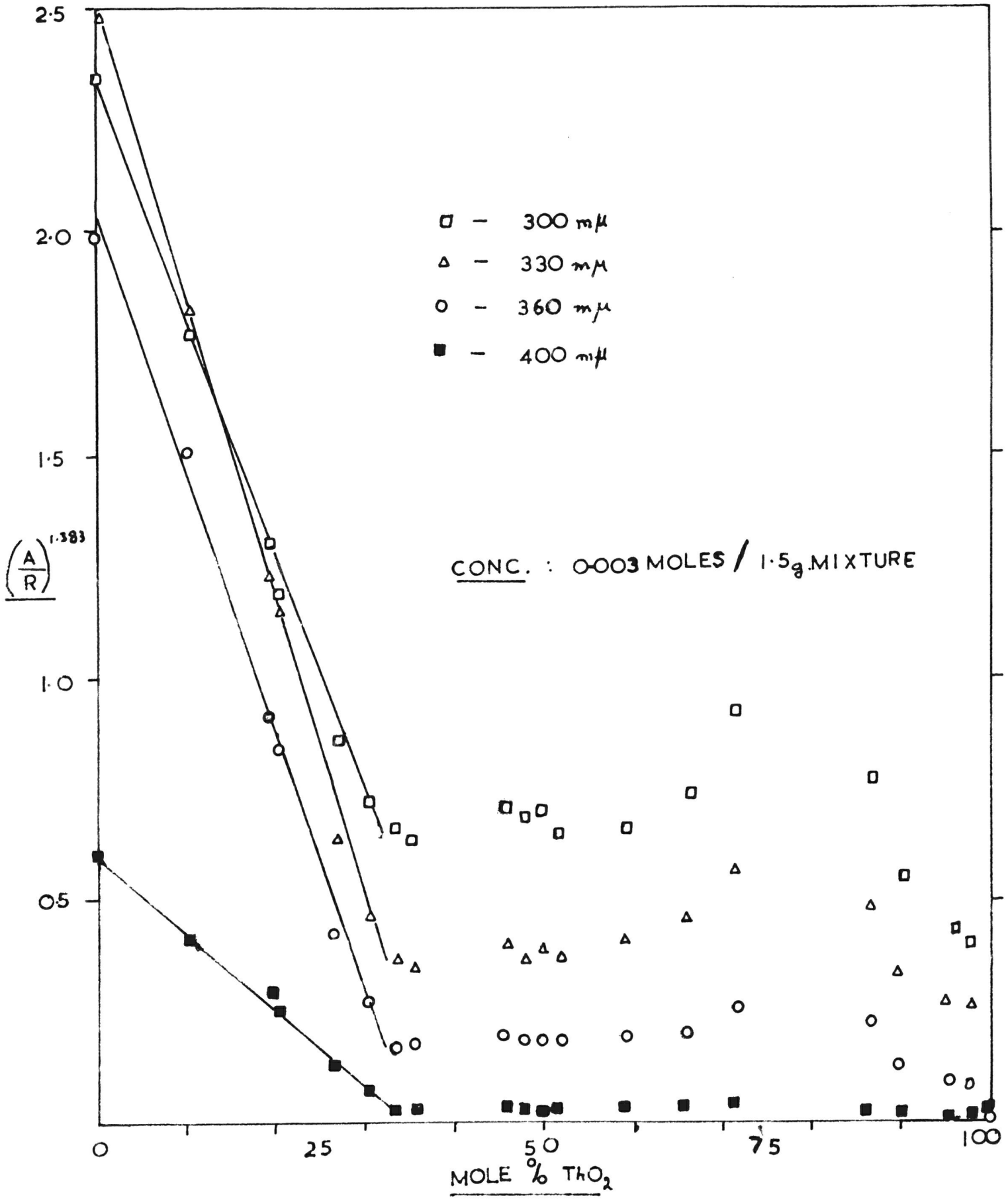


Table 27.

Increases in diameters of ThO_2/MoO_3 pellets on heating.

% ThO_2	△ d. (mm.)
0·00	0·0
10·44	0·5
19·96	1·7
20·68	1·9
27·47	2·9
30·52	3·3
33·38	3·8
35·47	3·5
46·38	2·5
48·63	2·0
50·07	1·7
59·48	1·2
66·45	0·9
72·86	0·6
87·24	0·1
100·00	0·0

The greatest swelling therefore occurred at 33% ThO_2 suggesting the formation of the normal molybdate. The fully reacted mixtures were diluted with MgO and their absorptions measured at 300, 330, 360, and 400mμ are plotted in Fig. 24: a break at 33% ThO_2 is evident in all cases showing the formation of $Th(MoO_4)_2$. The absorptions from 33-100% ThO_2 do not show the linear behaviour expected but this was not examined further.

The powder photographs of the reacted mixtures showed that only one compound was formed at 33% ThO_2. The diffraction lines observed are given in Table 28.

FIGURE 25

SPECTRUM OF MoO_3/ZrO_2

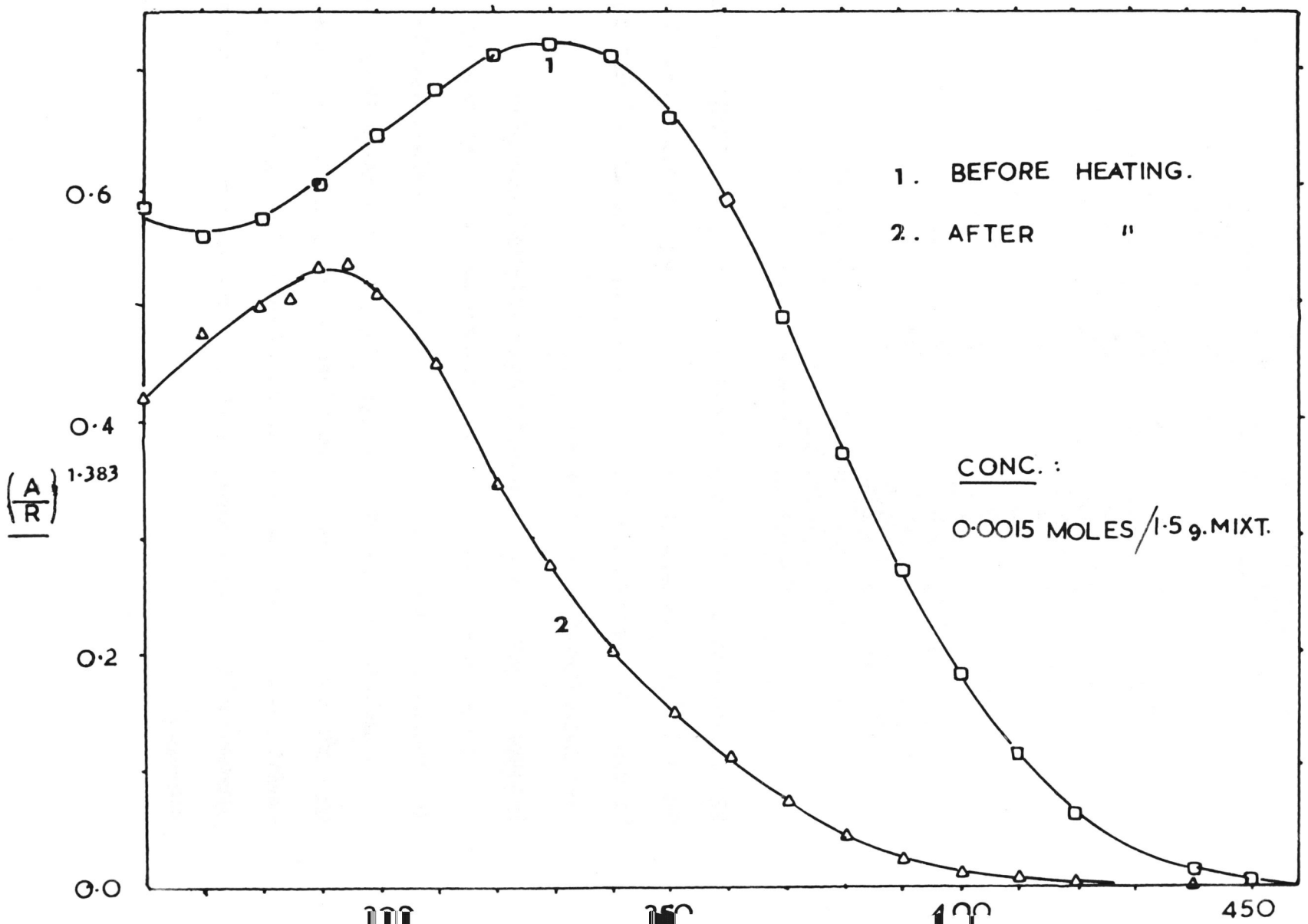


Table 28.

d spacings of $Th(MoO_4)_2$.

d (Å)	Intensity
5·03	100
3·76	20
3·53	100
3·13	15
3·07	15
2·95	15
2·26	5
1·98	20
1·93	10
1·90	10
1·84	20
1·75	20
1·685	10
1·538	10
1·459	5
+ 18 lines to 0·8337	⩽ 5

It is concluded that ThO_2 reacts with MoO_3 in the solid state to form $Th(MoO_4)_2$. The reflectance results in the 33-100% ThO_2 region suggest some interaction between this compound and ThO_2, but the x-ray study showed that mixtures in this range contained only $Th(MoO_4)_2$ and ThO_2.

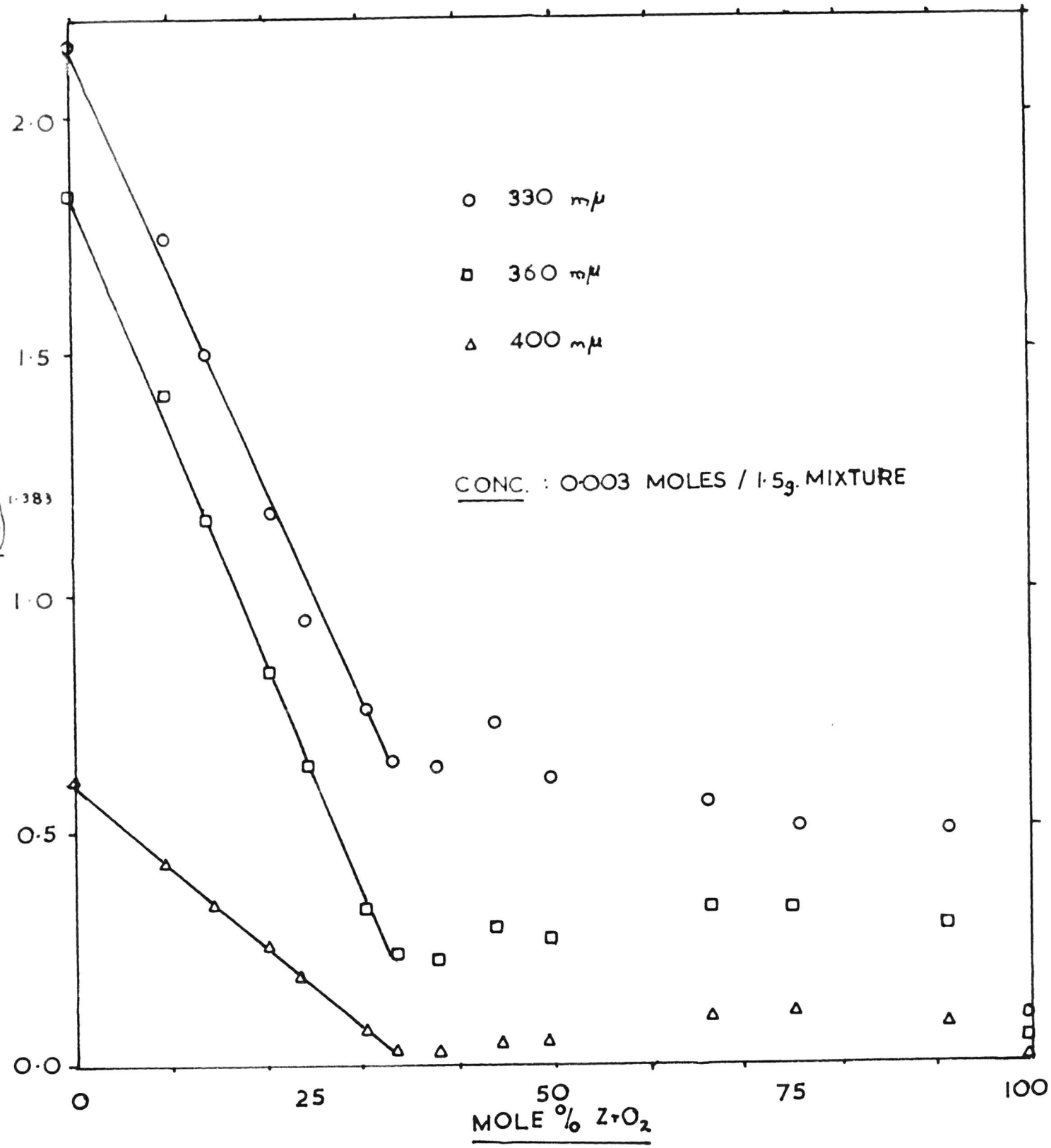
Reaction between Zirconium Dioxide and Molybdenum Trioxide:

Zirconium molybdate has been prepared as a gel from solution (Prakash,1932): no information exists on its preparation by solid state reaction.

A pelleted mixture of MoO_3 and ZrO_2 (2:1 molar respectively) was heated at 700°, and, as for the corresponding ThO_2-MoO_3 pellet, considerable swelling was observed and the yellow colour was no longer present. The spectrum of the heated mixture differed from the spectrum of the unheated mixture /

FIGURE 26

ABSORPTION PLOTS FOR MoO_3/ZrO_2



mixture as is shown in Fig. 25 showing that reaction had occurred: this was confirmed by the differences in the x-ray powder photographs of the two mixtures.

A series of mixtures was reacted by the standard procedure at 700°, and after the first heating period of two hours the diameters of the discs were measured. The swelling was considerably greater for this system than for the ThO_2/MoO_3 system and several of the heated discs were far from circular: an average diameter was measured. The increase in the diameter of the discs is shown in Table 29.

Table 29.

Increase in diameter of ZrO_2/MoO_3 pellets on heating.

% ZrO_2	△ d.(mm.)
0·00	0·0
9·52	1·1
14·08	1·4
20·53	2·5
23·73	3·1
30·68	4·3
33·40	6·3
38·34	5·0
44·85	4·3
49·92	3·7
66·52	1·2
75·68	0·6
91·12	0·1
100·00	0·0

The maximum increase in the diameter of the discs was observed at 33%, suggesting the formation of $Zr(MoO_4)_2$.

The reflectances of the mixtures were studied at 330, 360 and 400mμ and the composition/absorption plots are shown in Fig. 26. The break at 33% ZrO_2 in all cases confirms the formation of $Zr(MoO_4)_2$: again non-linear /

non-linear results were obtained in the 33-100% metal oxide region.

The x-ray study showed the presence of only one product at 33% ZrO_2. The photographs of the other reacted mixtures contained only those lines present in the 33% mixture and lines due to the appropiate excess reactant. The d spacings of the $Zr(MoO_4)_2$ lines are shown in Table 30.

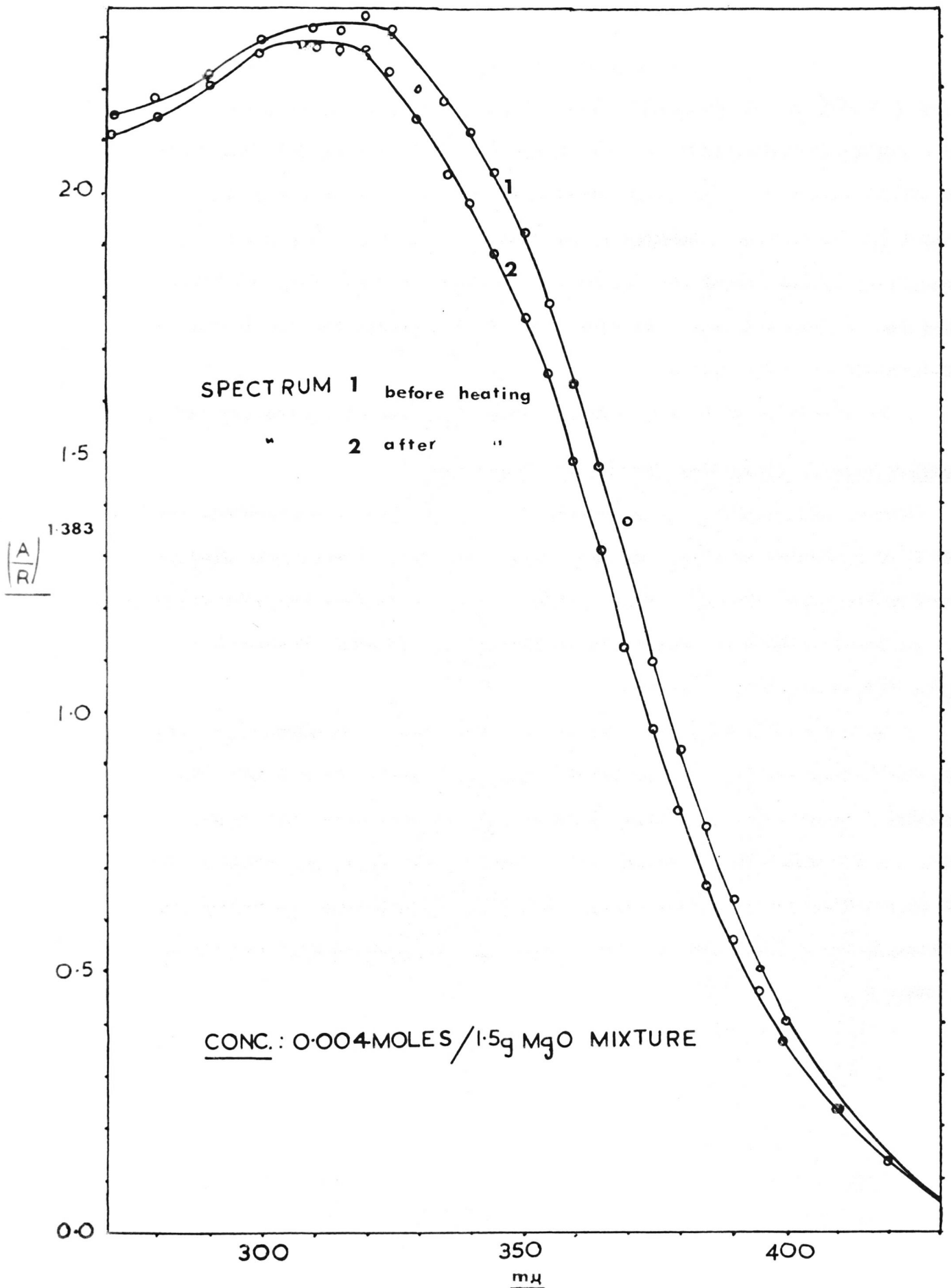
Table 30.

d spacings of $Th(MoO_4)_2$.

d (Å)	Intensity
3•836	100
2•906	60
2•518	30
2•315	20
1•907	20
1•813	30
1•680	15
1•616	10
1•603	10
1•458	20
1•402	5
1•364	20
+ 18 lines to 0•8008	≤ 20

It is concluded that solid state reaction takes place between ZrO_2 and MoO_3 on heating and that only one product $Zr(MoO_4)_2$ is formed. Again the variation of absorption in the 33-100% metal oxide region could not be explained on a basis of the formation of another product since the x-ray method gave no indication of this.

FIGURE 27: SPECTRUM OF MoO_3/B_2O_3



Reaction between Boric Oxide and Molybdenum Trioxide:

No information has been published on this system. Commercial boric oxide is a glass. On heating to 650° it did not, however, appear to melt and a pelleted mixture with MoO_3 was prepared and heated at this temperature. The pellet retained its original shape and colour and the spectrum was not changed by the thermal treatment as is shown in Fig. 27. The x-ray powder photographs of the heated and unheated mixtures were identical, all lines being due to MoO_3 and being accompanied by a dark background due to the non-crystalline boric oxide.

It is concluded that no reaction between B_2O_3 and MoO_3 occurs at 650°.

Reaction between Alumina and Molybdenum Trioxide:

Tamman and Westerhold (1925) found that the primary and secondary heating curves of a mixture of Al_2O_3 and MoO_3 were identical and concluded that no reaction had taken place. German (1931) titrated aluminium sulphate solution with sodium molybdate and found that a precipitate of molar composition Al_2O_3: MoO_3 = 1:2·61 was formed.

In this work it was found that solid state reaction between Al_2O_3 and MoO_3 does occur but that the standard heating procedure did not take the reaction to completion and longer heating periods were necessary to achieve this. A 25% molar Al_2O_3 mixture was heated for six days, grinding, sampling and repelleting at daily intervals. After about five days the absorption at any wavelength was not changed by further heating; typical results are shown in Table 31.

FIGURE 28

ABSORPTION PLOTS FOR MoO_3/Al_2O_3

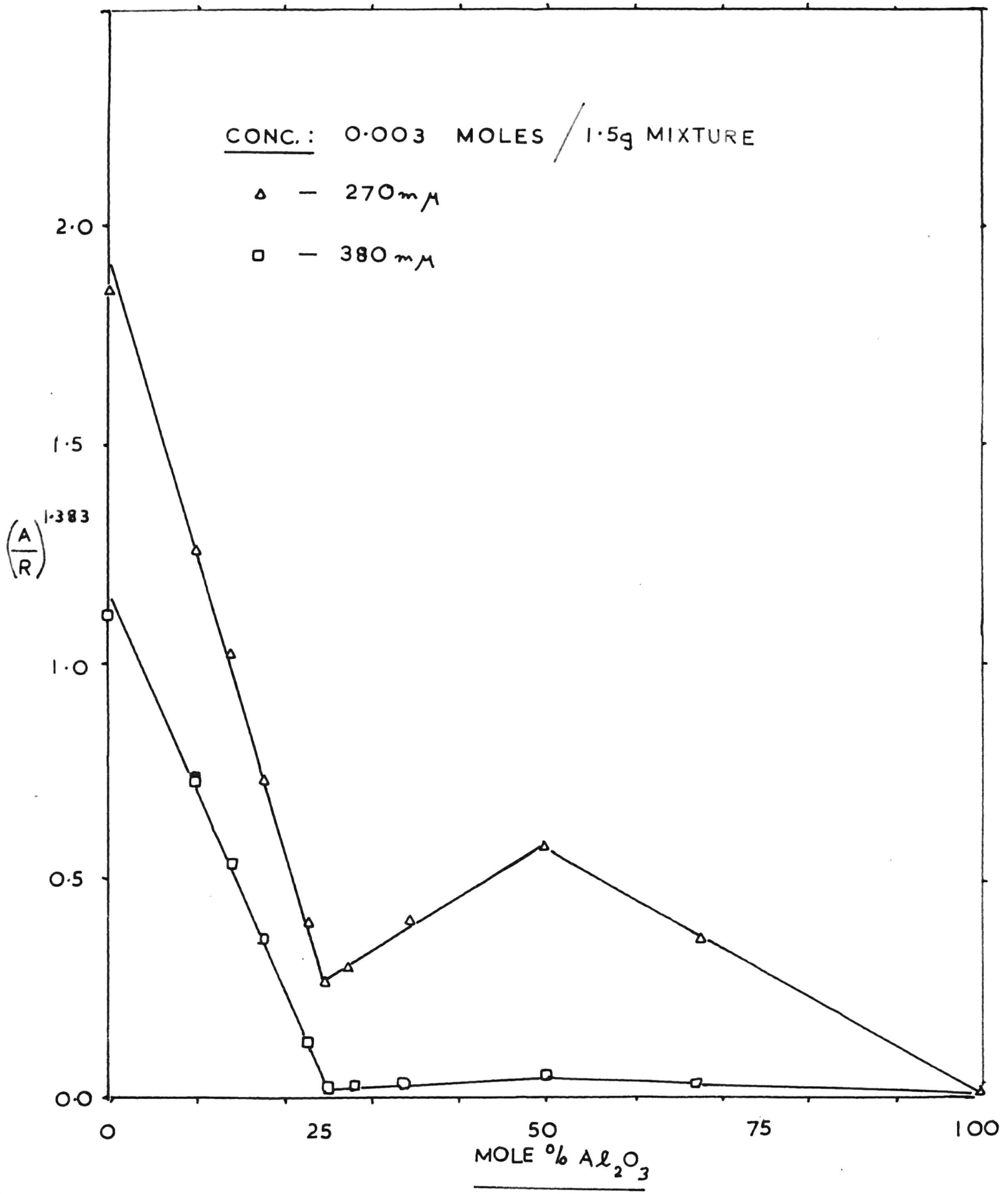


FIGURE 29

SPECTRA OF ALUMINIUM MOLYBDATES

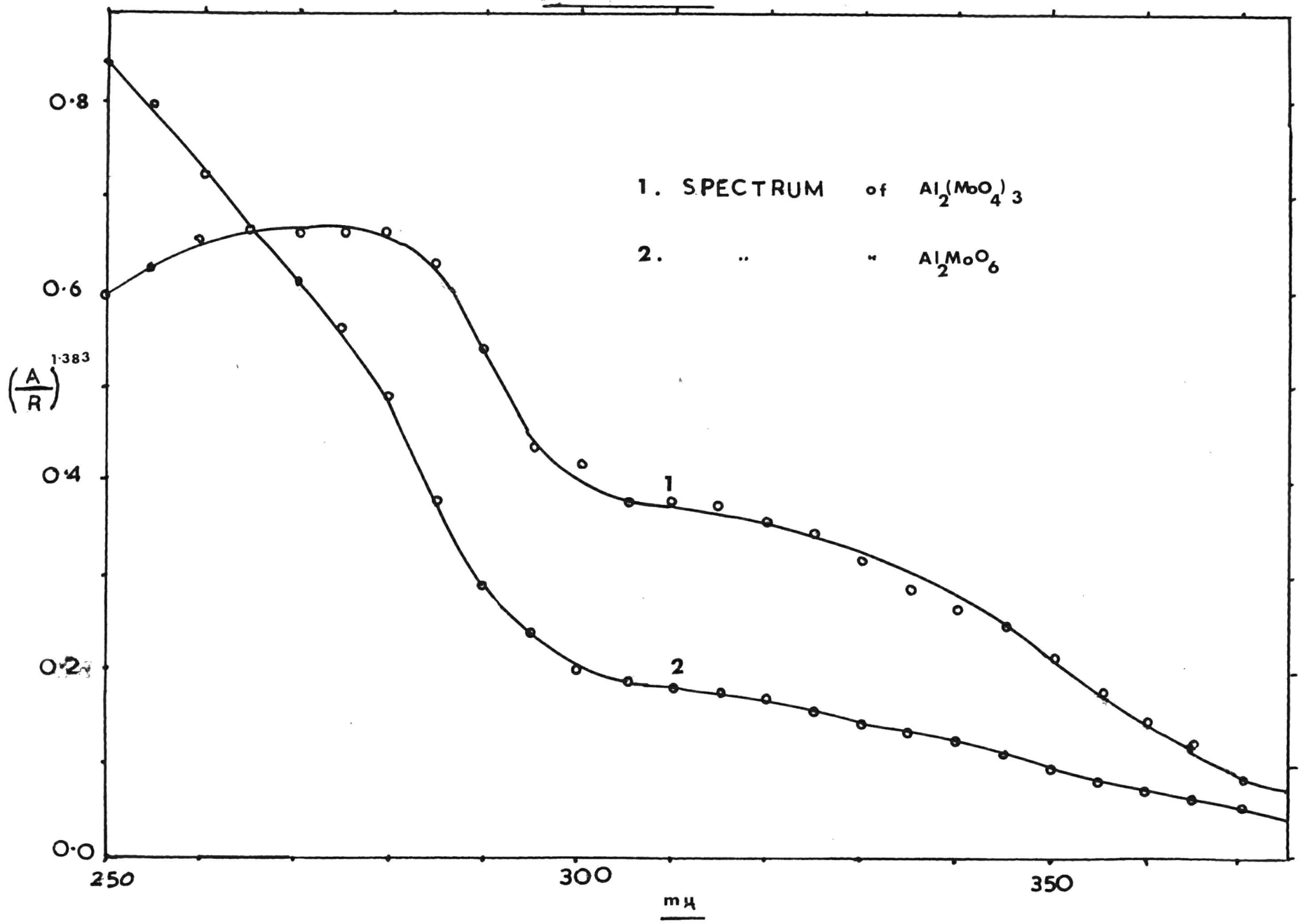


Table 31.

Absorption of Al_2O_3/MoO_3 on heating.

No. of days at 700°	$(\frac{A}{R})^{1.383}$	
	400mu	330mu
0	0·415	2·52
1	0·071	0·505
2	0·047	0·482
3	0·027	0·335
4	0·013	0·262
5	0·010	0·238
6	0·011	0·232

Mixtures of the oxides were therefore reacted at 700° for five days, grinding and repelleting at daily intervals. Reflectance measurements were taken at 270, 300, 330, 360, 380 and 400mu and typical plots are shown in Fig. 28. In all cases a break at 25% molar Al_2O_3 was obtained showing the formation of $Al_2(MoO_4)_3$ but in addition a break at 50% Al_2O_3 was observed particularly at 270 and 300mu: this suggests the formation of Al_2MoO_6. The spectra of the 25% and 50% Al_2O_3 reacted mixtures were quite different as is shown in Fig. 29: in the wavelength range studied Al_2O_3 does not absorb so that the differences can only be accounted for by another reaction product.

The x-ray powder photographs of the 15-70% Al_2O_3 mixtures contained no lines at all, only a very intense background being visible. The exposure time was reduced from 20 to 5 minutes and, though the heavy background was reduced, no lines were again visible.

It is concluded that solid state reaction between Al_2O_3 and MoO_3 takes place at 700°, but relatively slowly; this may be due to the high lattice energy of alumina. The normal molybdate $Al_2(MoO_4)_3$ and probably Al_2MoO_6 are formed though additional evidence is necessary to confirm the latter.

II. D. Systems in which more than one Product is formed.

The composition of the products formed by reaction of MoO_3 with PbO and with Bi_2O_3 were determined by the reflectance and x-ray methods. The systems were reacted by fusion to ensure the formation of all products which need not necessarily be true by solid state reaction.

The reactants were weighed directly into platinum crucibles, with the MoO_3 under the PbO or Bi_2O_3 to minimise the volatilisation of MoO_3. Preliminary experiments showed that more than two fusions had no further effect on the reflectance results and the following standard procedure was adopted:-

mixtures of the reactants were heated to 1080°, which is above the m.p. of the reported compounds in both systems, for 30 minutes, removed whilst molten and air quenched; the crucibles and contents were reweighed, the products ground, and the fusions repeated.

The loss in weight for most mixtures was negligible but for those containing excess MoO_3 it was appreciable and allowance was made in calculating the mole % metal oxide.

Pure MoO_3, and mixtures containing it in excess were light grey in colour after fusion. However, on heating to 650° overnight the MoO_3 reverted to its normal pale yellow colour without significent weight change. The grey colour may have been due to loss of oxygen from MoO_3, but the amount involved must have been very small.

Lead Monoxide - Molybdenum Trioxide System:

Jander (1928) found that the product formed by solid state reaction of PbO and MoO_3 always contained more PbO than could be accounted for by the formation /

FIGURE 30

ABSORPTION PLOTS FOR PbO/MoO_3

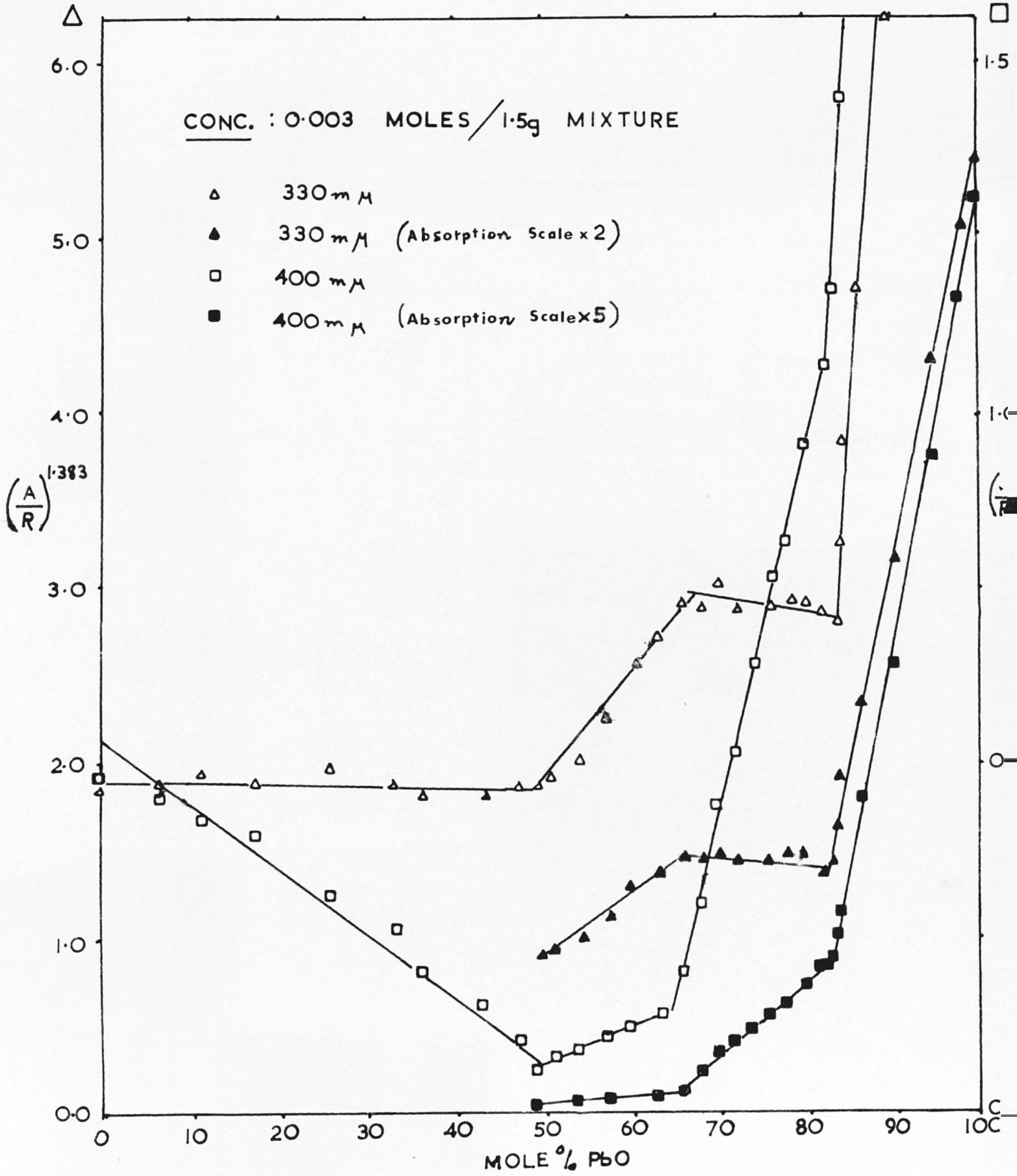
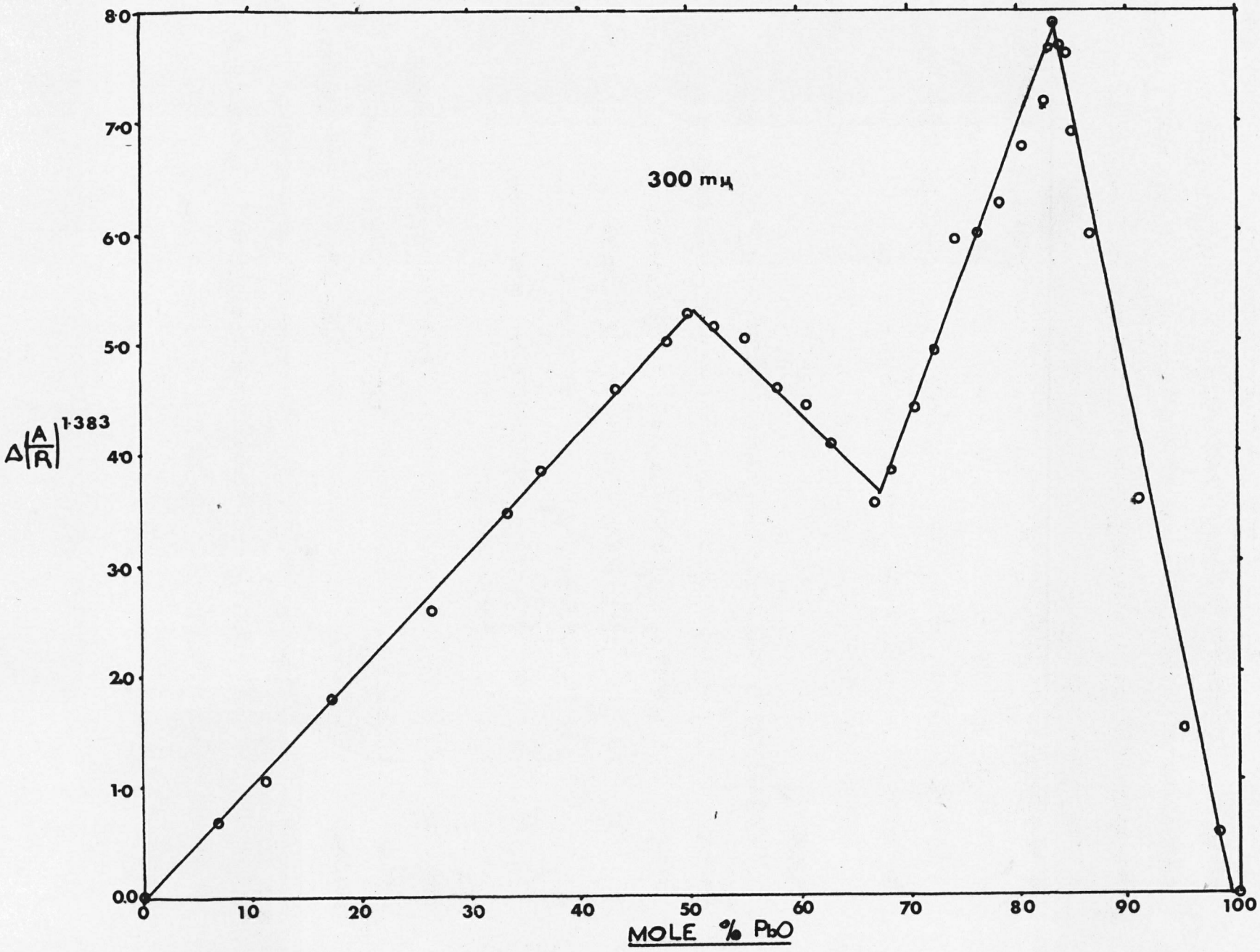


FIGURE 31

JOB'S PLOT FOR MoO_3/PbO



formation of the normal molybdate: he concluded that PbO is soluble in the molybdate. Sillen and Lundborg (1943) studied the fusion products by x-ray powder photography and reported the formation of $PbMoO_4$ and Pb_2MoO_5. They noted that the lattice dimensions of $PbMoO_4$ are the same whether it be in equilibrium with Pb_2MoO_5 or MoO_3 showing that solid solution does not occur in this range as suggested by Jander. No mention, however, is made by Sillen of the Pb_2MoO_5-PbO range. The thermal phase diagram of the system has been studied by Jaeger and Germs (1921) and more recently by Belyaev (1962) only the congruent compounds $PbMoO_4$ and Pb_2MoO_5 being found.

Mixtures of PbO and MoO_3 were reacted by the fusion procedure previously described.

Preliminary diffuse reflectance measurements showed, that to obtain readings in the absorption range over which the absorption function is most accurate, it was necessary to study the system in two parts:-

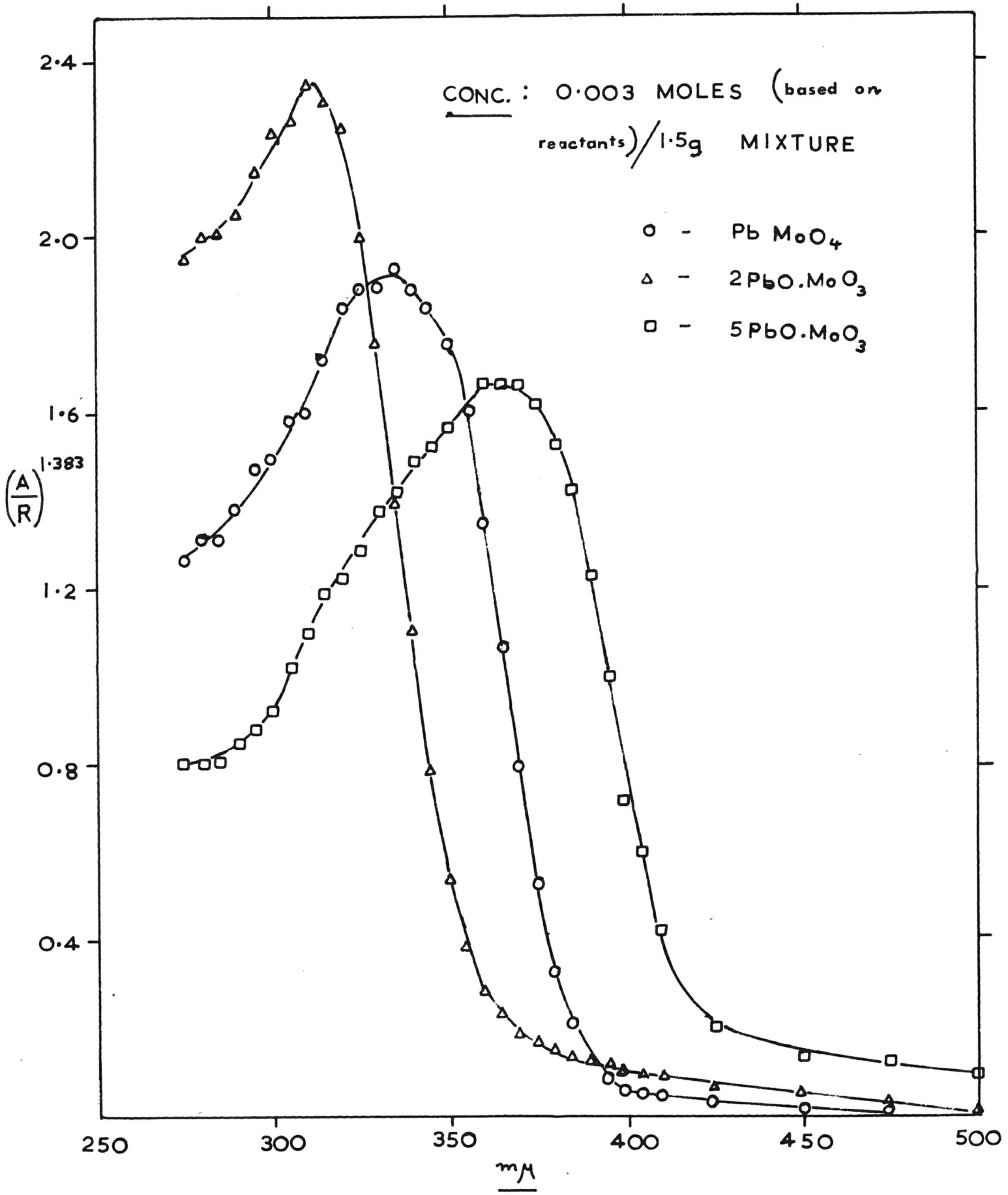
(i) From 0-72% PbO at a concentration of 0.003 moles per 1.500g. MgO mixture.

(ii) From 66.7-100% PbO at a concentration of 0.001 moles per 1.500g. MgO mixture.

Using the results obtained for the 66.7-72% PbO reacted mixtures in both series, the results of the second series were scaled to give absorptions corresponding to the concentration used in the first series. Measurements were made at 300, 330, 390 and 400mμ and an average of the results was taken from four surfaces. Direct absorption/concentration plots are shown at 330 and 400mμ in Fig. 30 and a Job's plot at 300mμ in Fig. 31. The figures /

FIGURE 32

SPECTRA OF LEAD MOLYBDATES



figures indicate the formation of three products at 50·5 ± 0·5, 67·2 ± 0·4, and 83·5 ± 0·3 % PbO, corresponding to PbO/MoO_3 ratios of 1·02 ± 0·02:1, 2·05 ± 0·03:1, and 5·05 ± 0·10:1. The results at the other wavelengths were consistent with the formation of these three compounds, whose spectra are shown in Fig. 32.

The reacted mixtures were studied by the x-ray method and the phases observed are shown in Table 32.

Table 32.

Phases in $PbO-MoO_3$ system.

Mole % PbO	Phases Observed
0·00	MoO_3
11·05	MoO_3 + R.P.1.
26·07	"
33·61	"
36·41	"
43·42	"
47·97	R.P.1.
50·06	"
51·82	"
54·76	"
57·99	R.P.1 + R.P.2
60·77	"
63·79	"
66·69	R.P.2
68·53	"
70·81	R.P.2 + R.P.3
74·17	"
78·08	"
80·57	"
82·23	R.P.3
83·42	"
84·33	"
86·46	R.P.3 + PbO
90·58	"
94·88	"
100·00	PbO

The composition of the three products formed R.P. 1, 2 and 3 cannot be expressed accurately from these results. The first two, however, are obviously $PbMoO_4$ and Pb_2MoO_5; the third lies in the possible PbO/MoO_3 molar ratio range of $5 \pm 1{\cdot}1{:}1$. The d spacings of the three products are given in Table 33.

Table 33.

d spacings of Lead Molybdates.

$PbMoO_4$		Pb_2MoO_5		$5\,PbO.\,MoO_3$	
d	I	d	I	d	I
3·18	100	3·40	100	3·17	100
2·92	30	3·01	100	2·85	30
2·64	30	2·89	50	2·67	30
2·34	5	2·41	50	1·97	50
2·06	5	1·893	20	1·89	20
2·00	80	1·780	20	1·72	50
1·91	30	1·650	80	1·660	30
1·77	80	1·530	100	1·645	30
1·642	80	0·830	20	1·580	10
1·605	30	0·812	20	1·360	10
1·348	15	0·804	20	1·288	10
1·314	30	0·776	20	1·268	20
1·300	60			1·208	20
1·246	20			1·163	5
1·232	20			1·138	5
1·208	20			1·124	10
1·183	20			1·083	10
1·150	20			1·060	10
1·122	30			1·051	10
+ 18				0·940	20
lines to	30				
0·7735					

The quality of the photograph of the $Pb_2 MoO_5$ was poor: the lines were broad and were accompanied by a heavy background. The $Pb MoO_4$ and $5 PbO.MoO_3$ have similar d spacings for the strongest lines, suggesting that they have similar or at least related lattice dimensions: the $Pb_2 MoO_5$ has quite different d spacings.

It is concluded that in the $PbO-MoO_3$ system three compounds are formed on fusion: in addition to the two products $Pb MoO_4$ and $Pb_2 MoO_5$ previously reported a third having a PbO/MoO_3 ratio of 5:1 has been found. As this compound was not reported by Sillen and Lundborg, it is suggested that their study was restricted to the range 0 -67% PbO.

Reaction of Bismuth Oxide with Molybdenum Trioxide:

The literature on the compounds formed between Bi_2O_3 and MoO_3 is conflicting: compounds claimed to be formed by one worker being refuted by others. Zambonini (1920) was the first to claim the formation of $Bi_2(MoO_4)_3$ in an anhydrous condition but his preparation has been criticized and it was suggested that in fact he prepared $NaBi(MoO_4)_2$ (Sillen, 1943). Phase diagram studies by Belyaev (1962) have shown that three well defined compounds are formed:- $Bi_2(MoO_4)_3$, $Bi_2O_3.MoO_3$, and $3 Bi_2O_3.MoO_3$ but as Belyaev notes, this does not exclude the possibility that other compounds can exist in the solid state. Gattow (1958) claims to have formed $2 Bi_2O_3.MoO_3$ from solution, reporting it as a mixed oxide with the cubic CaF_2 type structure with a the cell dimension equal to $5{\cdot}65 \pm 0{\cdot}01$ A. Sillen and Lundborg (1943) studied the fusion products of Bi_2O_3 and MoO_3 by x-ray powder photography and in all, five compounds are claimed:-

1) /

1) ≏ 9 Bi_2O_3.MoO_3; 2) ≏ 3 Bi_2O_3.MoO_3; 3) 4) two phases whose compositions are not specified; 5) $Bi_2(MoO_4)_3$. The lines observed in the powder photographs or the number of mixtures studied are not recorded but phases 1) and 2) are said to be tetragonal (a = 5·497, c = 5·572) and cubic (a = 5·635) respectively; the latter has almost the same cell dimensions as Gattow's 2 Bi_2O_3.MoO_3. In the same publication (Sillen, 1943) the study of the WO_3/Bi_2O_3 system is reported. The cell dimensions of the WO_3 compounds are similar to those quoted for the MoO_3 compounds above but Sillen notes that a number of weak lines were observed which cannot be accounted for unless the real cell is larger (this would appear necessary at least for the compounds containing 18 Bi atoms per Mo or W atom); single crystal studies of $Bi_2(WO_4)_3$ (Sillen 1943) indicated that the unit cell was 6 times as large (apparent cell from powder studies, tetragonal a = 5·426Å, c = 5·464Å; real cell from single crystal studies, tetragonal a = 7·674Å = 5·426Å$\sqrt{2}$, c = 16·39Å = 3 x 5·466Å) but he was unable to grow crystals of the other reported phase for a similar study. In the present work the fusion products were studied by the x-ray powder and reflectance methods.

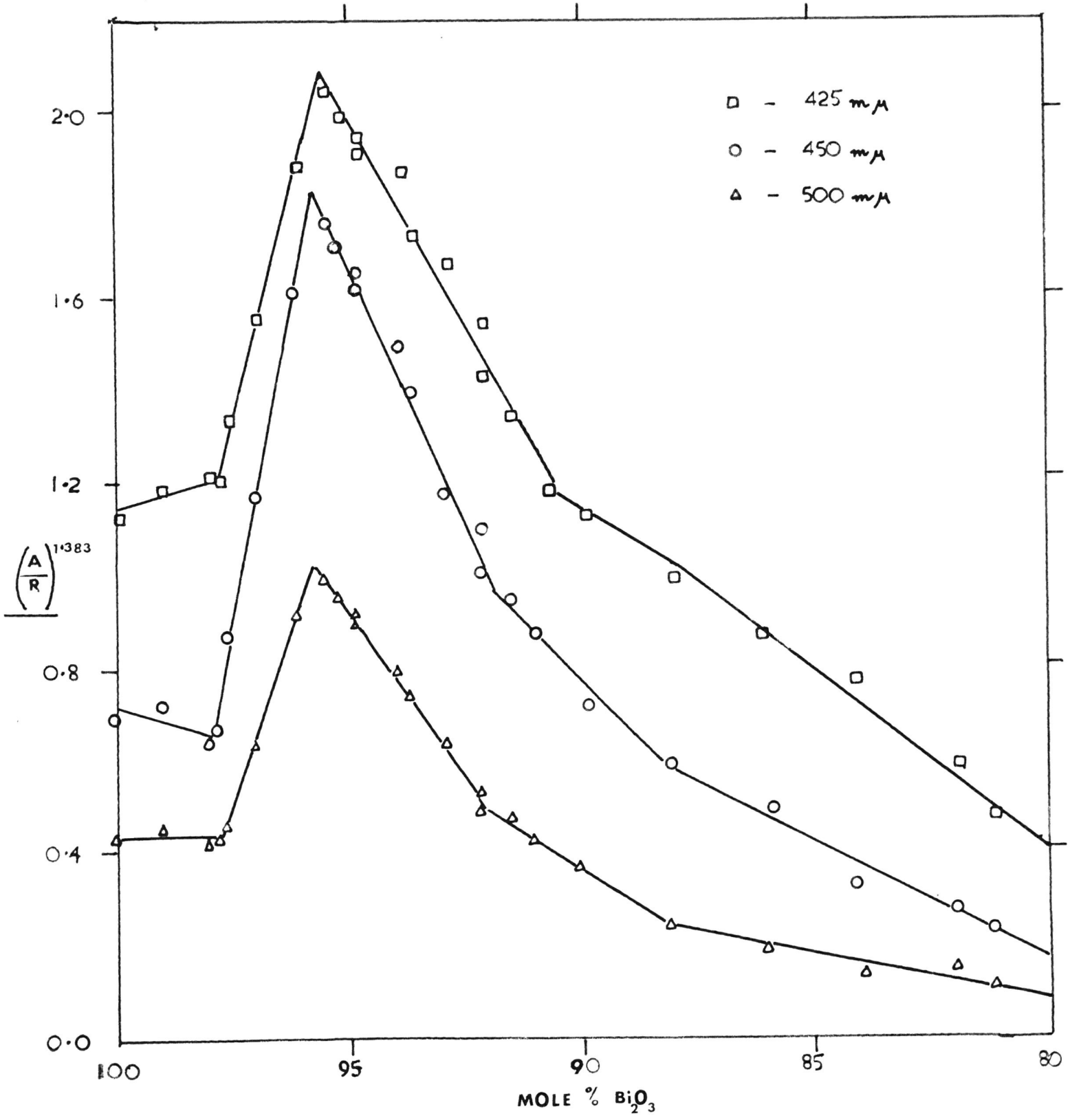
The Bi_2O_3 - MoO_3 mixtures were fused by the techniques previously described and air-quenched. The colour of the reacted mixtures was similar for the most part but those around 90 - 96% Bi_2O_3 were intense brown-red in colour, as opposed to the light brown colour of the others.

Preliminary spectral studies revealed that the absorption measurements in the ultraviolet region changed little with composition and so measurements for the greater part were restricted to the visible region. For convenience the /

FIGURE 33

COMPOSITION — ABSORPTION PLOT

FROM 100 – 80 % Bi_2O_3



the reflectance results are subdivided into three parts 1) from 100-80% Bi_2O_3, 2) 85-45% Bi_2O_3, 3) 50-0% Bi_2O_3.

1) 100-80% Bi_2O_3 region:

The composition/absorption plots at 500, 450 and 425mμ are shown in Fig. 33 and the compositions, which give maxima or minima in absorption and recorded in Table 34.

Table 34.

Phases in the range 100-80% Bi_2O_3.

Phase	Composition Break (% Bi_2O_3)		
	500mμ	450mμ	425mμ
1	97·8	97·8	97·9
2	95·7	95·6	95·5
3	± 92·5	± 92·5	± 91·6
4	± 89·0	± 89·0	-

The phases at 97·8 and 95·6% were not expected on the basis of previous publications. The sharpness of the absorption change at these compositions, however, would appear to establish that definite compounds of these compositions exist. The compositions of the third and fourth phases are not established with great accuracy due to the relatively small change of slope.

2) 85-45% Bi_2O_3 region:

Within this region the measured absorption at 500mμ was small and no reliance could be placed on it: the region of most rapid absorption change was 400-450mμ and the absorption composition plots at three wavelengths in this /

FIGURE 34 REGION 85 — 45 % Bi_2O_3

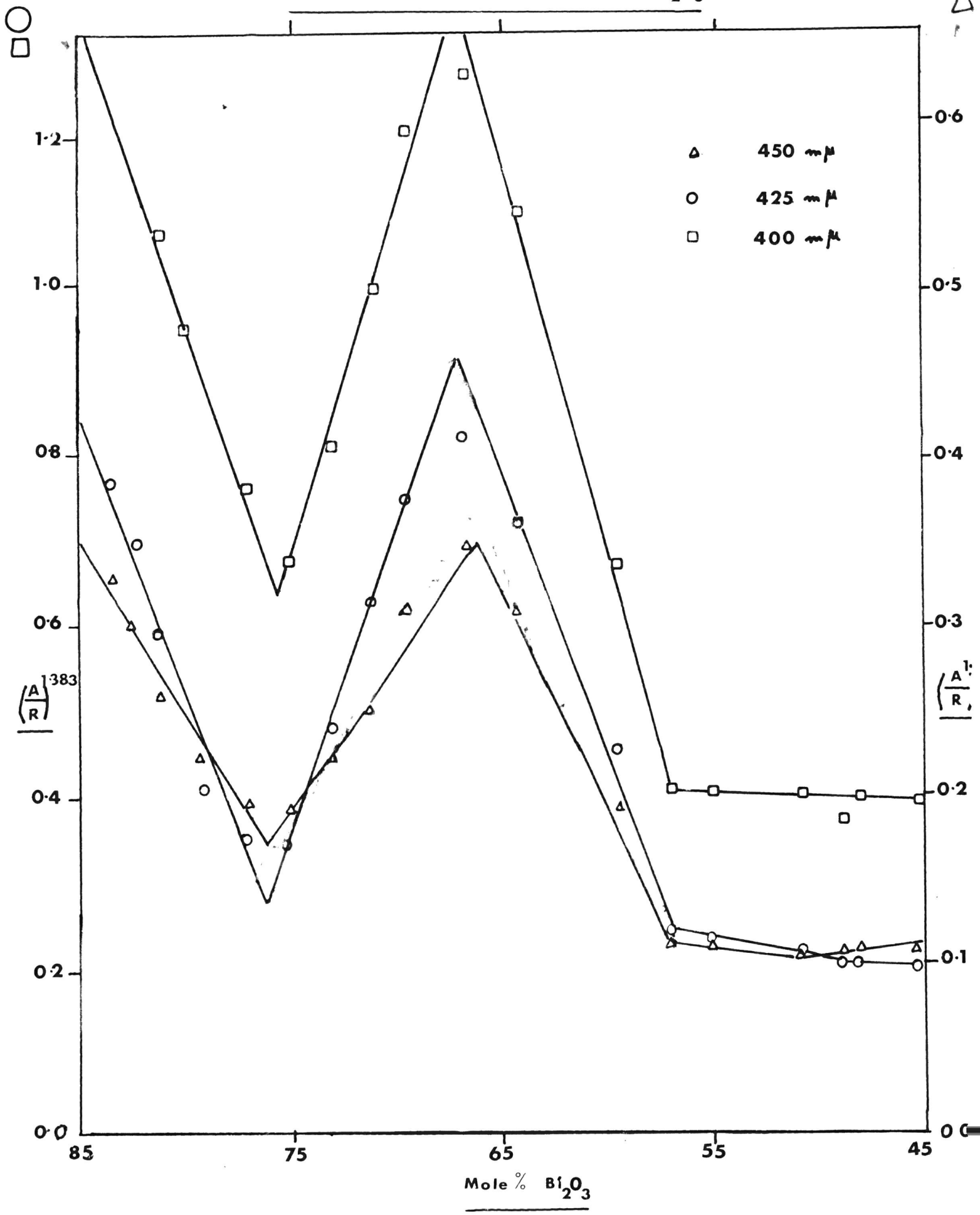
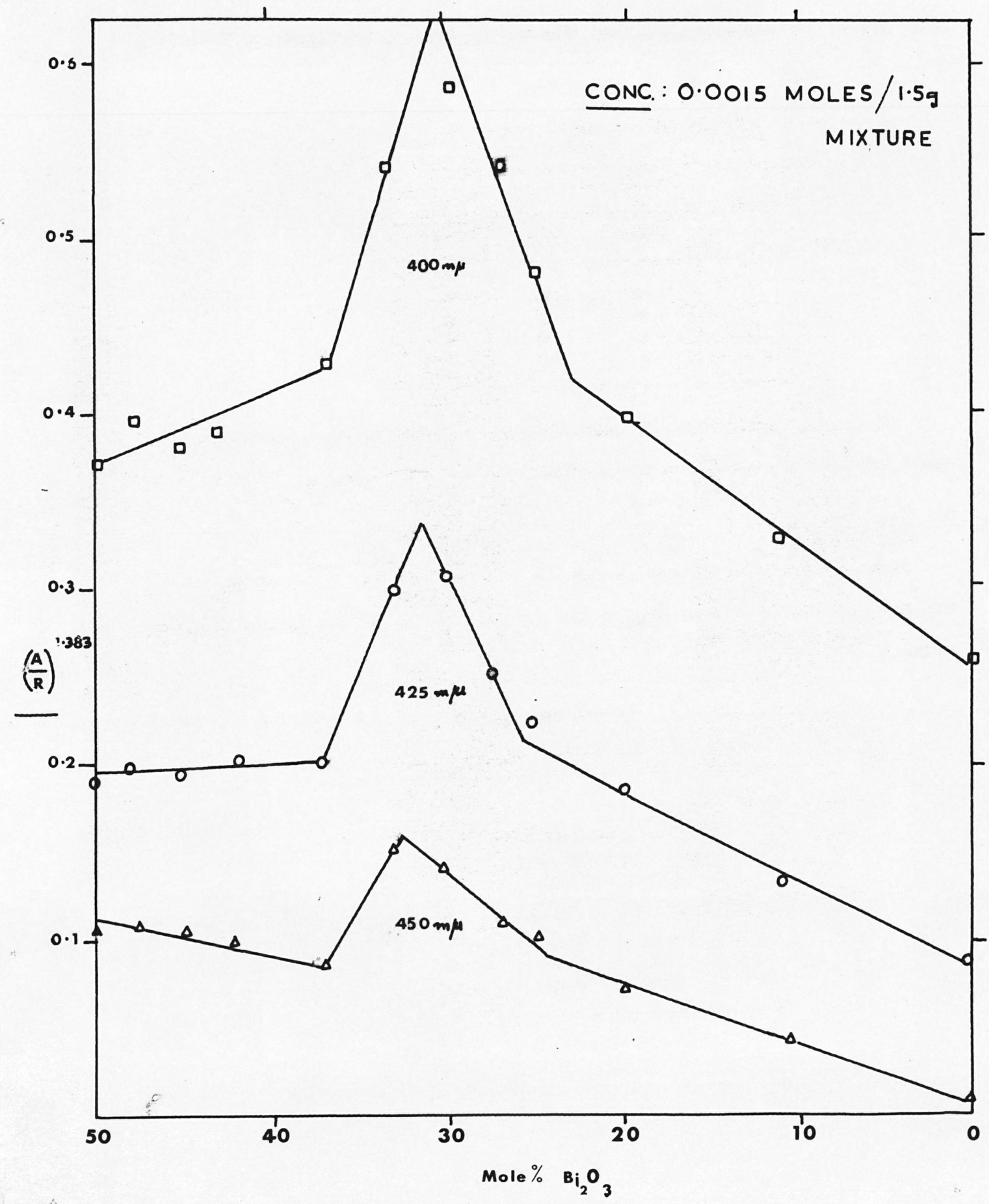


FIGURE 35

REGION 0 - 50% Bi_2O_3



this region are shown in Fig. 34: the phases observed are given in Table 35.

Table 35.

Phases in the range 85-45% Bi_2O_3.

Phase	Composition Break (% Bi_2O_3.)		
	400mμ	425mμ	450mμ
5	75·2	75·5	75·5
6	67·2	66·7	66·6
7	56·5	56·2	56·5
8	-	≙ 50	≙ 50

It is surprising that the break at 50% Bi_2O_3 was rather indefinite since this corresponds to the established compound $Bi_2O_3.MoO_3$.

3) 50-0% Bi_2O_3:

Again the wavelength range 400-450mμ was found the most useful and typical plots are shown in Fig. 35 and the composition of the phases observed given in Table 36.

Table 36.

Phases in the range 50-0% Bi_2O_3.

Phase	Composition Break		
	400mμ	425mμ	450mμ
9	38·0	37·0	≙ 37
10	31·2	32·0	≙ 32·5
11	22·6	24·3	≙ 22·1

The compositions of the phases were not established with accuracy in this region since the absorption changes are relatively small.

X-ray Study:

In the Bi_2O_3 photograph 63 lines were observed, several of which were probably doublets and the d spacings and intensities of the first 15 are shown in Table 37.

Table 37.

d spacings of Bi_2O_3.

d(Å)	Intensity
3·22	100
2·67	80
2·52	10
2·38	5
2·23	5
2·12	5
1·945	30
1·864	10
1·830	5
1·736	10
1·726	10
1·662	10
1·650	10
1·580	10
1·564	10

These are in agreement with α-Bi_2O_3 as recorded by Sillen (1941) and Frondel (1943) but a number of additional lines were observed in this study. From 100-96% Bi_2O_3 changes were observed. The photographs around 96% Bi_2O_3 contained fewer lines and in addition several new lines appeared, the strongest being of d-spacing 2·82, 1·97, 1·604 though many of the remaining lines /

lines coincided with lines in the Bi_2O_3 photograph. This confirms the formation of either phase 1 or 2. The differences in the photographs in the range 96 - 25% Bi_2O_3 were slight as is apparent from Table 38, which lists the d spacings down to 1·25 of four reacted mixtures.

Table 38.

d spacings of several Bi_2O_3/MoO_3 reacted mixtures.

% Bi_2O_3			
94·8	75·0	50.9	25·0
3·20	3·19	3·21	3·20
	3·08		3·08
			2·85
2·82			2·82
2·71			
		2·03	2·01
1·97	1·99	1·99	1·97
1·94			1·90
1·71	1·73	1·72	1·72
1·67	1·68	1·69	1·71
		1·64	1·65
			1·60
			1·56
1·27	1·29	1·28	1·28
1·25	1·27	1·25	1·25

The lines common to all mixtures were generally the strongest and it is concluded that the compounds formed in this system have similar or related crystal lattices. The lines peculiar to certain ranges were generally weak and as a result it was impossible, visually at least, to determine the compositions at which they appeared. It is not surprising that Sillen and Lundborg were unable to define the phases present in this range.

Mixtures /

Mixtures from 0-20% Bi_2O_3 were found to contain MoO_3 lines suggesting the formation of the normal molybdate, $Bi_2(MoO_4)_3$.

As described above a large number of mixed oxides have been found in the Bi_2O_3 - MoO_3 system by the diffuse reflectance technique, the molar compositions and Bi:Mo ratios of which are shown in Table 39.

Table 39.

Phases in Bi_2O_3/MoO_3 System

Phase	Mole % Bi_2O_3	$\frac{Bi}{Mo}$ ratio
1	97·8 ± 0·2	89 ± 8
2	95·6 ± 0·2	43 ± 3
3	92 ± 1	23 ± 3
4	≏ 89	≏ 16
5	75·4 ± 0·2	6·12 ± 0·08
6	66·9 ± 0·3	4·04 ± 0·06
7	56·5 ± 0·3	2·60 ± 0·04
8	≏ 50	≏ 2
9	≏ 37	≏ 1·2
10	≏ 32·5	≏ 0·96
11	≏ 24	≏ 0·65

This list includes all the previously reported compounds: phase 4 is Sillens 9 $Bi_2O_3.MoO_3$ within the limits stated by him; phase 5, 3 $Bi_2O_3.MoO_3$ has been reported by Sillen and also by Belyaev; phase 6 is Cattow's 2 $Bi_2O_3.MoO_3$; phases 8 and 11 are the established $Bi_2O_3.MoO_3$ and $Bi_2(MoO_4)_3$ respectively. The two unspecified phases reported by Sillen are probably two of the phases from 6 - 9. Sillen (1937, 1945) has reported the formation of other mixed oxides of bismuth of general formula $M^{IV}_2 Bi_{24}O_{40}$ or $M^{III}_2 Bi_{24}O_{39}$, the /

the formulae being deduced from the disappearance of the α-Bi_2O_3 lines in reacted mixtures. The x-ray powder photographs of these compounds were interpreted in terms of body-centred cubic compounds of the lattice dimensions shown in Table 40.

Table 40.

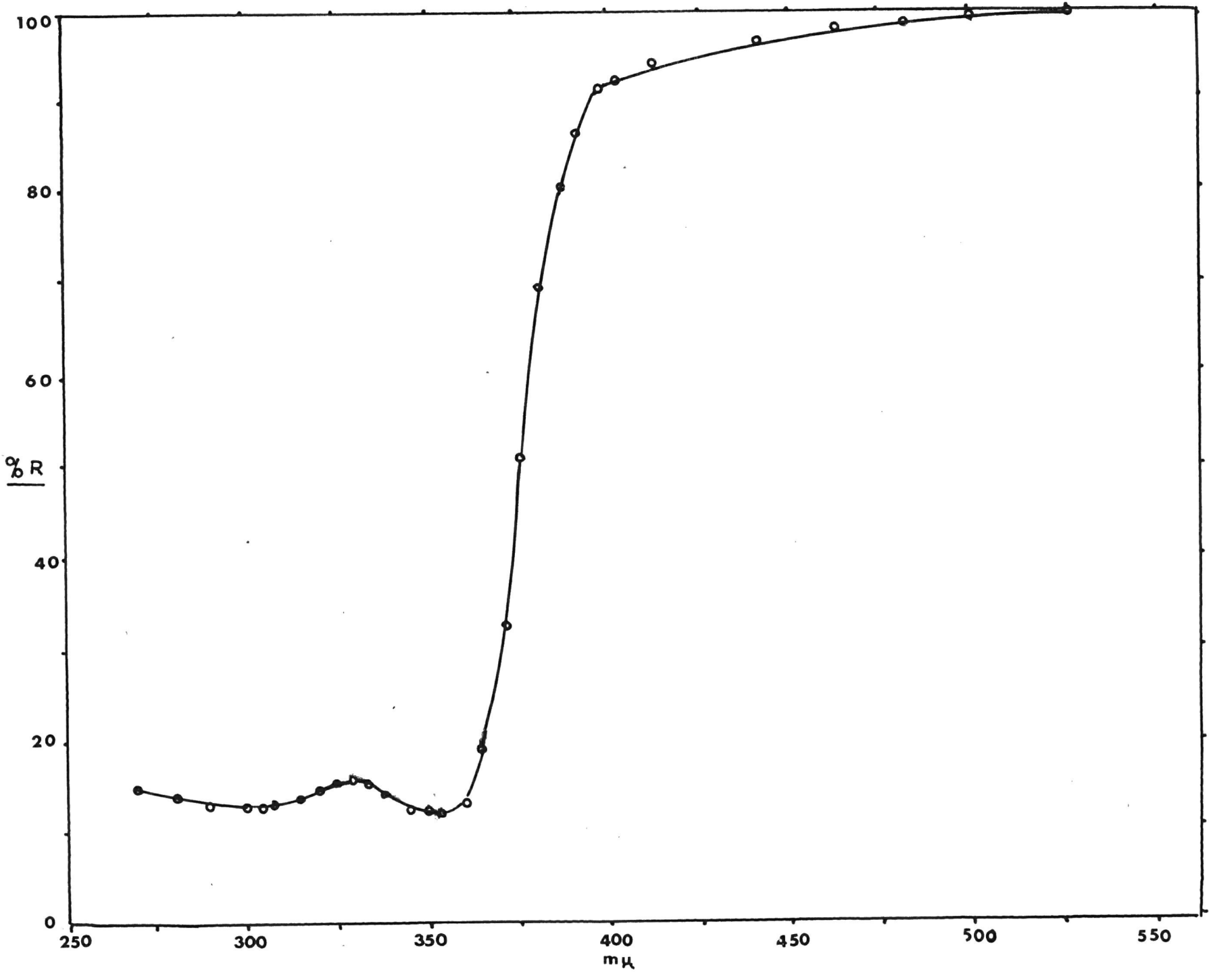
Metal	a (Å)
Al^{3+}	10·14
Tl^{3+}	10·15
Fe^{3+}	10·16
Si^{4+}	10·08
Ce^{4+}	10·20
Zr^{4+}	10·21
Pb^{4+}	10·23

The so called γ-Bi_2O_3 is said to be similar in structure (Sillen, 1937) having a body centred cubic lattice (a = 10·243A), with 26 Bi atoms per unit cell. Two of the Bi atoms occupy special positions at the centres of spheres of 12 Bi atoms and Sillen suggested that it is these special positions which are occupied by the foreign atoms in the above compounds. There still appears some doubt about the number and structures of the high temperature forms of Bi_2O_3 (Wells, 1962_b) and in order to explain the existence of the compounds formed with Mo along similar lines it is necessary to assume that there are other form(s) of Bi_2O_3 with very large unit cells with special positions which the Mo can occupy. Development along these lines, however, is too hypothetical and additional information is called for. This

could /

could only be obtained by x-ray methods, preferably of single crystals grown from the melt.

FIGURE 36 : SPECTRUM OF LEAD BROMIDE



III. Miscellaneous Studies by Diffuse Reflectance Spectrophotometry.

In this section a number of studies, all of which are directly or indirectly relevant to thework of previous sections, are reported. For mixtures of lead halides with potassium halides it was found that quantitative analysis by the diffuse reflectance procedure is not possible but, from spectral studies, the reason for this is traced to interaction of the constituents. The influence of the thermal treatment of a solid on its reflectance spectrum is reported for copper monoxide. Solid state reaction of MoO_3 with sintered copper oxide is compared with the reaction using the non-sintered oxide. Finally, the influence of solid solution of two substances on their reflectance spectra is reported for the $PbBr_2$-$PbCl_2$ system.

III.A. Mixtures of Lead Halides with Potassium Halides.

The potassium halides (bromide and iodide) were of Analar grade and the lead halides (chloride, bromide and iodide) were prepared by precipitation from lead acetate solution by addition of a solution of the appropriate potassium halide. All substances were dried at 120°, ground in an agate mortar, and sieved through a 200/(B.S.) mesh sieve.

For all combinations of these halides of lead and potassium a limiting absorption could not be obtained on grinding.

$PbBr_2$/KBr mixtures:

The reflectance spectrum of pure $PbBr_2$ shown in Fig. 36 has two absorption maxima at 305 and 353mμ of approximately equal intensity. Several mixtures of $PbBr_2$ in KBr were prepared and the % absorption measured /

measured at 300 and 350mμ after grinding for various intervals. Typical results are shown in Table 41 for a 3·00% $PbBr_2$ mixture.

Table 41.

Effect of Grinding on % absorption.

Grinding Time (Minutes)	% Absorption	
	300mμ	350mμ
0	24·6	35·0
15	39·2	38·0
30	52·9	32·2
45	57·9	27·3
60	65·7	24·0
75	69·3	22·6
90	69·0	21·2
120	72·0	20·0

A limiting % absorption was not obtained for other mixtures in a practicable time; in all cases the absorption at 300mμ continued to rise steadily whilst that at 350mμ after an initial rise decreased steadily. Even on shaking the mixtures on a vibrational shaker the absorption changed as is apparent from Table 42 which gives the results obtained for a 3·00% $PbBr_2$ mixture.

PS

FIGURE 37

SPECTRA OF $PbBr_2/KBr$ MIXTURES

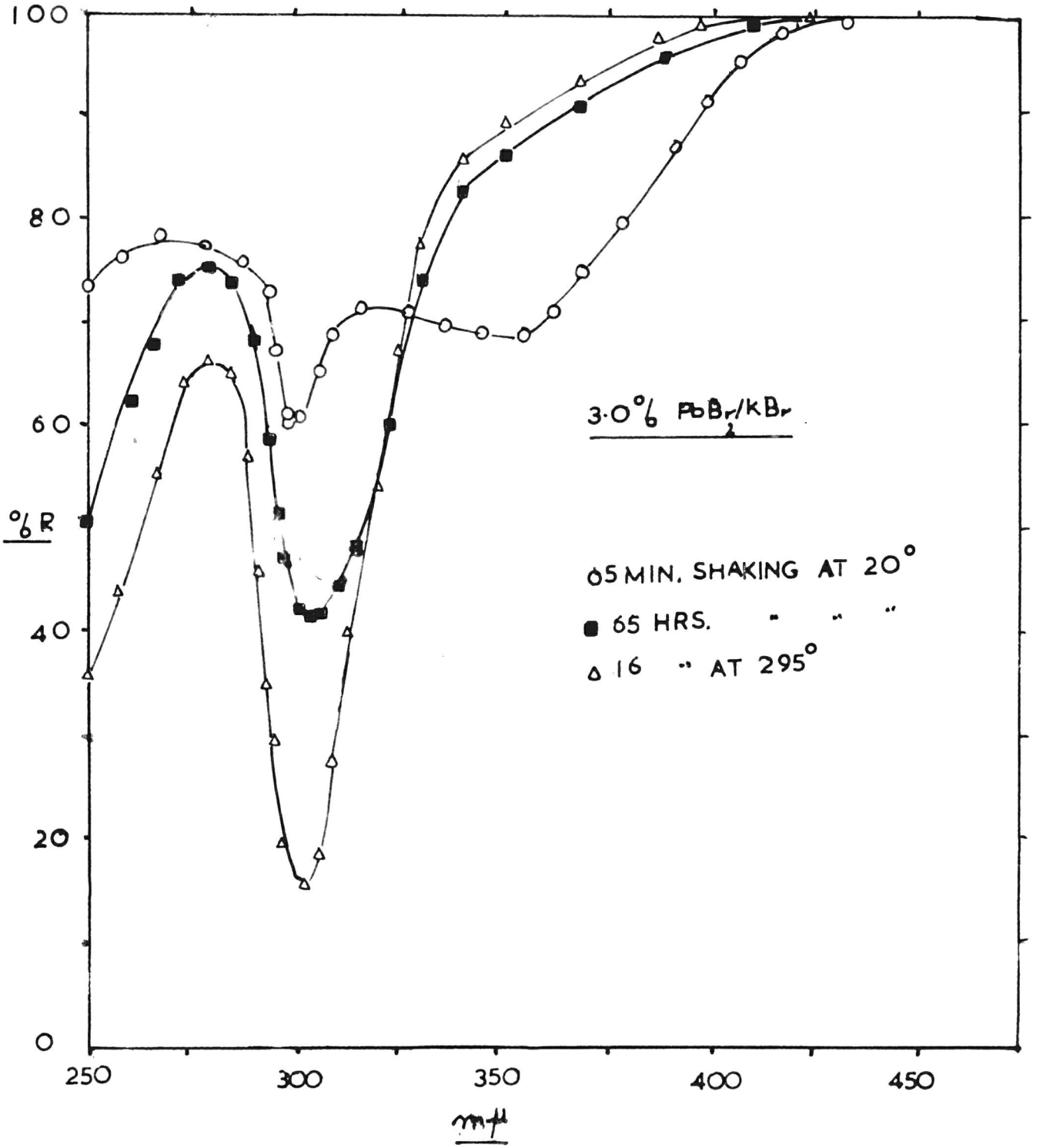


Table 42.

Effect of Shaking on % Absorption.

Shaking Time (Minutes)	% Absorption	
	300mμ	350mμ
5	24·2	34·0
60	42·0	33·9
240	45·1	32·1
1440	54·0	30·0
7200	60·0	25.0

The changes in absorption were also effected by heating the mixtures.

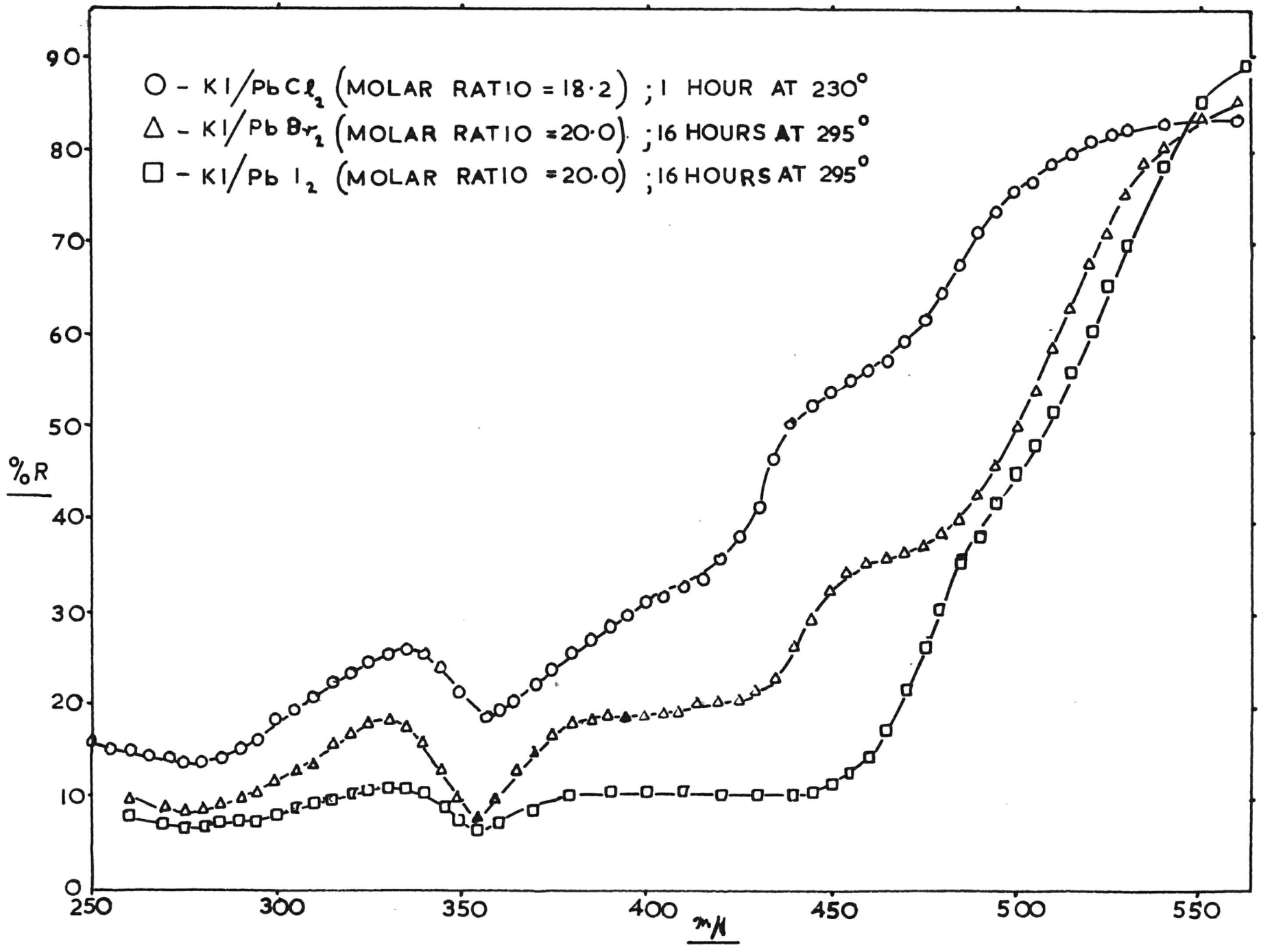
A diffuse reflectance spectrum study of several mixtures treated by either grinding, shaking or heating up to 300° revealed the development of a sharp absorption band with a maximum at 300-301mμ, and another strong absorption band in the ultraviolet, whose maximum was outwith the instrument range; in addition the $PbBr_2$ absorption band with a maximum at 353mμ progressively disappeared. Examples of the measured spectra are given in Fig. 37. Spectra of this type have been previously observed for $PbBr_2$ in KBr solution (Fromherz and Lih, 1931) and for $KBr/PbBr_2$ mixed crystals prepared by fusion (Hilsch, 1927; Rexer, 1937) and the features are compared with the present work in Table 43.

Table 43.

Spectral Features of $PbBr_2/KBr$.

Feature	This Work	Solution	Mixed Crystals
First Max.	300-2mμ	303mμ	302mμ
Second Max.	not observable	223·5mμ	223mμ

FIGURE 38 SPECTRA OF Pb HALIDE/KI MIXTURES



The absorption bands are obviously associated with the Pb^{++} ion in a bromide ion environment and since the spectrum in solution is virtually identical to that of the mixed crystals, the Pb^{++} ion environment would be expected to be the same in each case. Fromherz and Lih (1931) were of the opinion that the absorption in solution was associated with the $[PbBr_4]^{--}$ ion. For thallium bromide/potassium bromide phosphors it has been shown that the Tl replaces K in the K Br lattice and therefore has an octahedral environment of six bromide ions. Seitz (1938) thought that this is not the case with Pb but suggested no definite alternative; from these spectral considerations it would appear that the Pb^{++} ion is associated with four bromides. However, whether this is true or not, the results from this study show that $PbBr_2$ reacts with K Br at room temperature, presumably by diffusion into the K Br lattice.

Mixtures of KI with $PbCl_2$, $PbBr_2$ and PbI_2 :

The mixtures behaved in a similar manner to the bromide mixtures: that reaction occurred on grinding or shaking in the case of mixtures of K I with $PbCl_2$ or $PbBr_2$ was clearly indicated by the development of a yellow colour from the colourless solids. As the reactions proceeded the following features, as is shown in Fig. 38, become more pronounced:- a strong continous absorption with an edge of 520-530mμ and two sharp absorption features with maxima around 355mμ and 270mμ. The continous absorption is due to PbI_2 and the positions of the maxima agree with those previously observed in a solution of PbI_2 in K I (Fromherz and Lih, 1931) as is shown in Table 44.

Table 44.

Absorption Maxima of Pb halide/K I Mixtures.

Feature	This Work			PbI_2/K I solution
	$PbCl_2$	$PbBr_2$	PbI_2	
First Max.	358mμ	354mμ	360mμ	359-63mμ
Second Max.	276 mμ	274mμ	270mμ	272mμ

Fromherz and Lih also obtained an inflection at 308mμ in the spectra which was not obtained here. The similarity of the spectra of mixtures of lead halides with K I and the solution spectra of PbI_2 in K I suggests that the absorption bands arise from the Pb^{++} ion in an iodide environment. This provides evidence for the diffusion of the Pb^{++} ion from the lead halide into the K Br lattice since the final spectrum was largely independent of the lead halide commenced with.

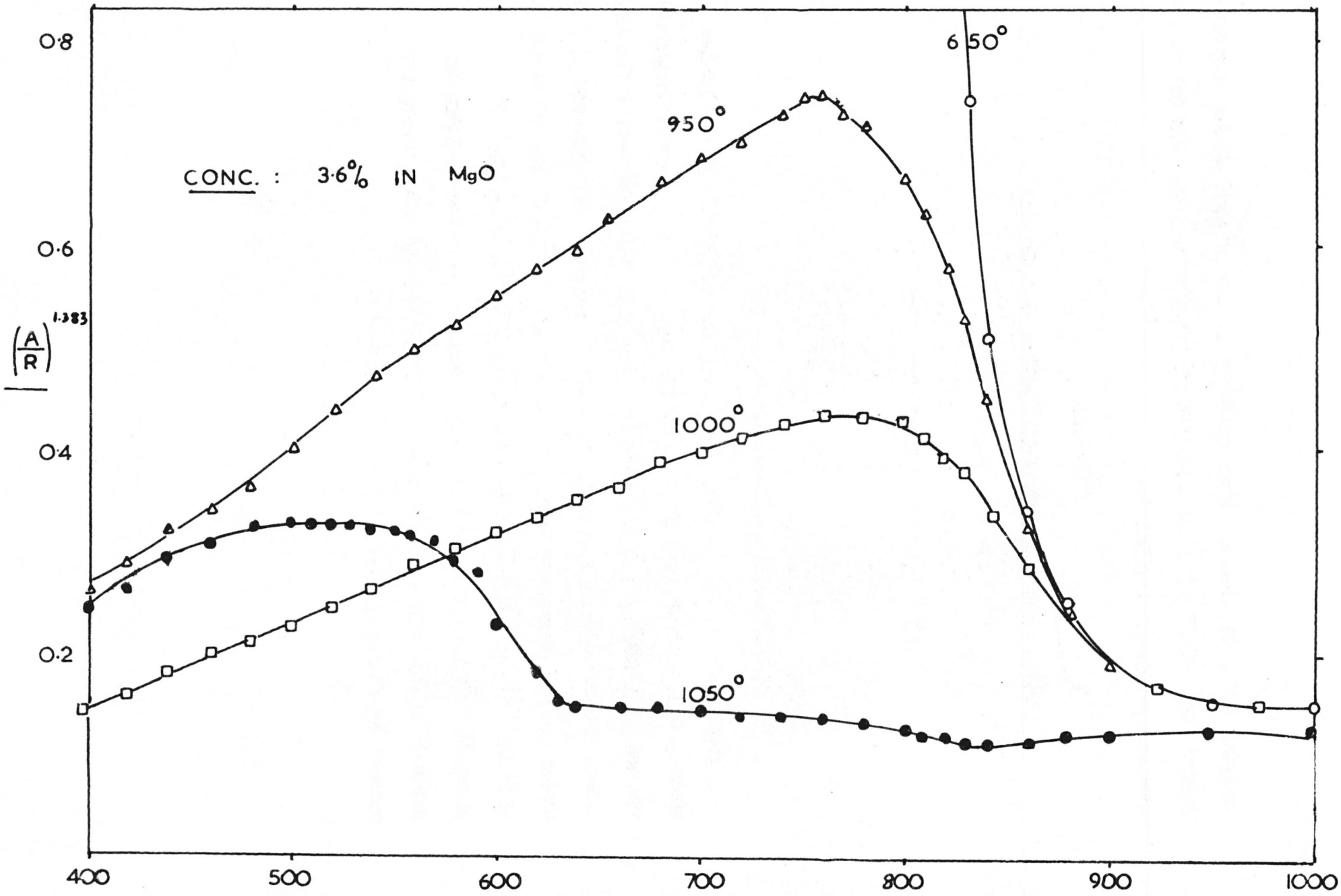
III. B. Thermal Treatment of Copper Oxide.

The changes in the reflectance spectrum of CuO on sintering are reported, and the reactions of the sintered and non-sintered oxides with MoO_3 are compared.

Analar CuO was heated to 650° for 24 hours, and weighed portions of this material were heated at various temperatures up to 1080° for 24 hours. A considerable decrease of volume occurred for the oxides heated to 950° and 1000° and the products assumed a grey, rather metallic, appearance whereas the original /

FIGURE 39

SPECTRUM OF CuO HEATED AT SEVERAL TEMPERATURES



original oxide was black. This contraction also occurred in the samples heated above 1000° but these were reddish-brown in colour. The weight losses obtained are given in Table 45.

Table 45.

Weight losses of CuO at different temperatures.

Temperature	% Wt. Loss
650°	< 0.01
850°	0.09
950°	0.21
1000°	0.16
1040°	9.96
1080°	10.02

The reaction $2\ CuO \longrightarrow Cu_2O + \frac{1}{2} O_2$ requires a weight loss of 10.04%, showing that in this study Cu_2O is formed above 1040°. At lower temperatures the weight losses are not significant. The reflectance spectra of the heated oxides were measured and several are shown in Fig. 39; the spectrum of CuO heated at 650° showed no change and was similar to that of the CuO heated at 700° for 24 hours, which has been previously given in Fig. 13. The absorption maximum of the CuO gradually shifted from 625mμ to 775mμ on increase of temperature. The main differences in the CuO spectra, were however in intensity, as is illustrated in Table 46.

FIGURE 40

SPECTRUM OF CuO HEATED AT 1000° FOR VARIOUS TIMES

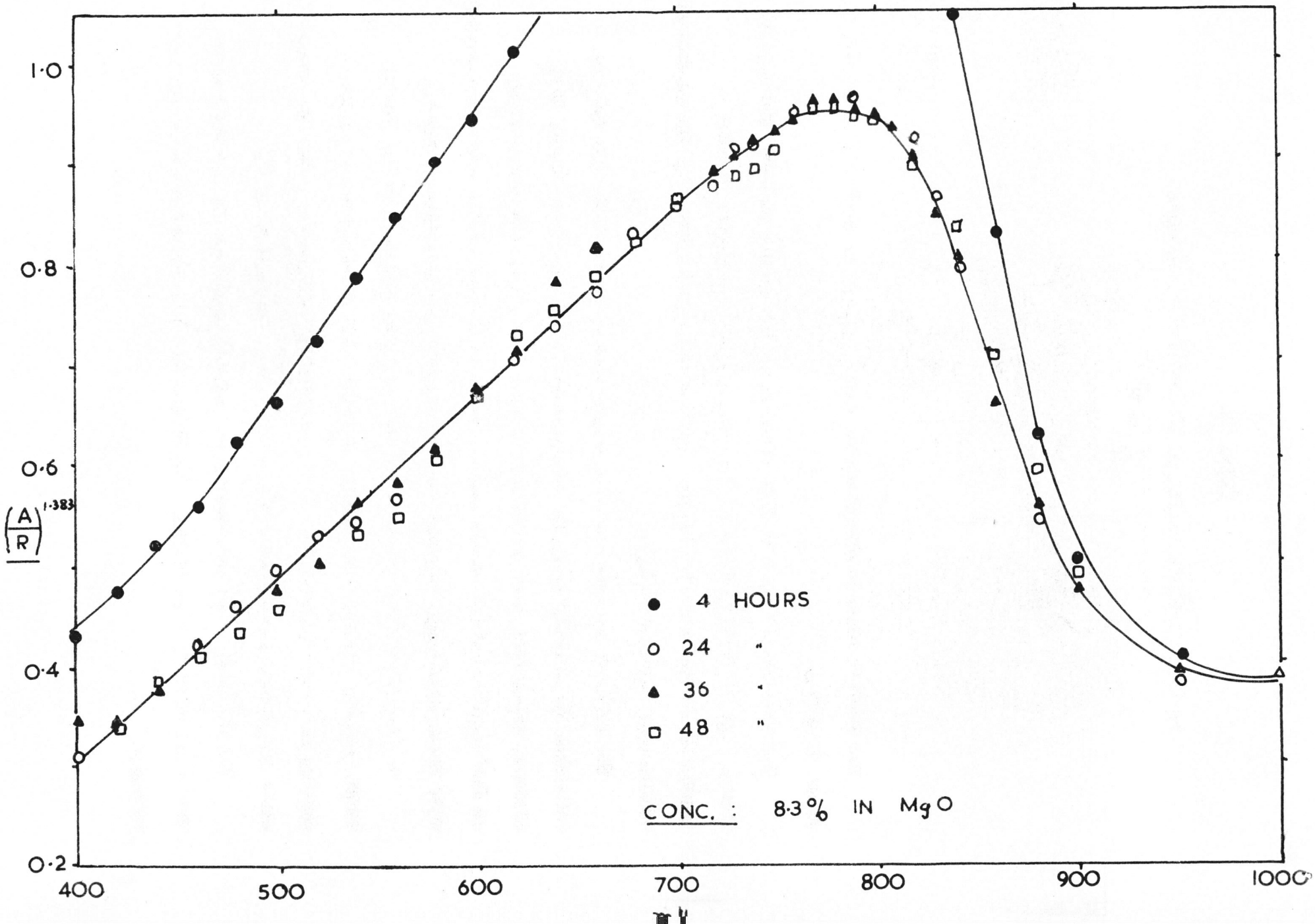


Table 46.

Absorption of CuO heated at differing temperatures.

Temp.	$(\frac{A}{R})^{1.383}$	
	650mμ	750mμ
650°	7·00	4·20
850°	3·40	2.02
950°	0·610	0·745
1000°	0·360	0·420

The cuprous oxide products showed a new absorption band with a maximum at about 500mμ.

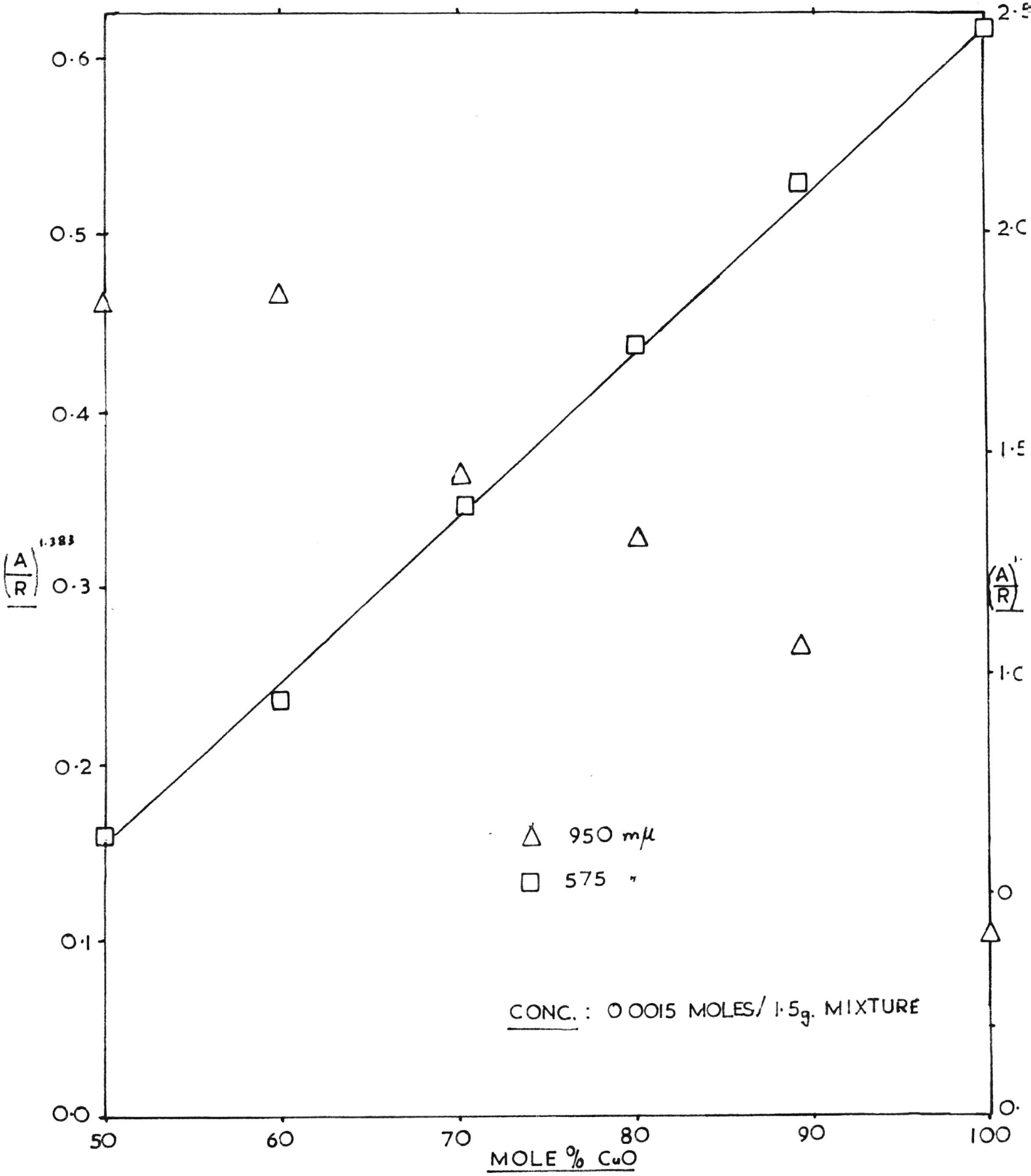
The spectrum of CuO was also measured after heating at 1000° for various times. As is shown in Fig. 4D the spectrum did not change further on continued heating after 24 hours: this was taken as indicating the completion of sintering at this time.

The sintered and non-sintered copper oxides were heated with MoO_3 to determine the minimum reaction temperatures and in addition several MoO_3 mixtures containing from 50-100 mole % of the sintered CuO were reacted at 650° under standard conditions and the absorptions of the products compared with those previously obtained for the non-sintered reaction products.

Equimolar pelleted mixtures of the MoO_3 with CuO were heated for 24 hours, and the minimum temperatures at which the pellets acquired a green colour, showing the formation of the molybdate, were noted. For the sintered oxide reaction commenced at 540°, and for the non-sintered 460°.

The absorptions of the reacted mixtures formed from the sintered oxide were studied at 575 and 950mμ. At 575mμ, at which copper oxide is the most strongly /

FIGURE 41: ABSORPTION PLOT FOR SINTERED CuO/MoO_2



strongly absorbing species, the composition/absorption plot, shown in Fig. 41, approximates to linear variation. For the unsintered oxide it has been previously noted that linearity was not observed. However, a scatter of points was again observed at 950mμ at which wavelength the product absorbs strongly. The significance of these observations is later discussed.

III. C. Lead Chloride-Lead Bromide Mixed Crystals.

Lead chloride and lead bromide are orthorhombic with four molecules per unit cell and belong to the space group V_h^{16}, (Brakken, 1932). Their lattice constants differ from the mean value by less than 3% and they would be expected to form a continuous series of solid solutions. The thermal diagram of the system supports this (Calingaert et al., 1949) but it has been noted by Nieuwenkamp and Bijvoet (1933) that in these isomorphous compounds the halide ions occupy two inequivalent positions in the crystal lattice which were designated x^i and x^{ii}, the first having the smaller space volume, and they suggested that a preferential replacement of the Cl^{ii} ions takes place in mixed crystals containing from 0-50% $PbBr_2$, leaving only the Cl^i ions for replacement from 50-100% $PbBr_2$. Evidence for this preferential replacement compound $PbCl^iBr^{ii}$ was obtained by Calingaert (1949) who found from x-ray studies that the plot of the lattice constants and unit cell dimensions of the solid solutions against mole % $PbBr_2$ showed a discontinuity at 50%. The present work was undertaken to substantiate the evidence for the formation of PbBrCl and to examine the changes in the reflectance spectrum of this compound when in solid solution with $PbBr_2$ or $PbCl_2$. The study was, however, undertaken before the quantitative diffuse reflectance method /

method had been developed and is therefore of a qualitative nature, in which the variation of the wavelengths of maximum absorption with composition is studied.

The solid solutions were prepared by fusion of the $PbBr_2$ and $PbCl_2$ in a nitrogen atmosphere to prevent the formation of the oxyhalides. The solutions were cooled slowly to aid crystallisation though according to the findings of Calingaert this is unnecessary. The reflectance spectra of the products were measured relative to a $MgCo_3$ block and in all cases two maxima in absorption were observed. For the products of high chloride content, measurements were necessary in the inaccurate 260-270mμ region; the wavelengths of these second maxima were however repeatable. The observed maxima in absorption are recorded in Table 47.

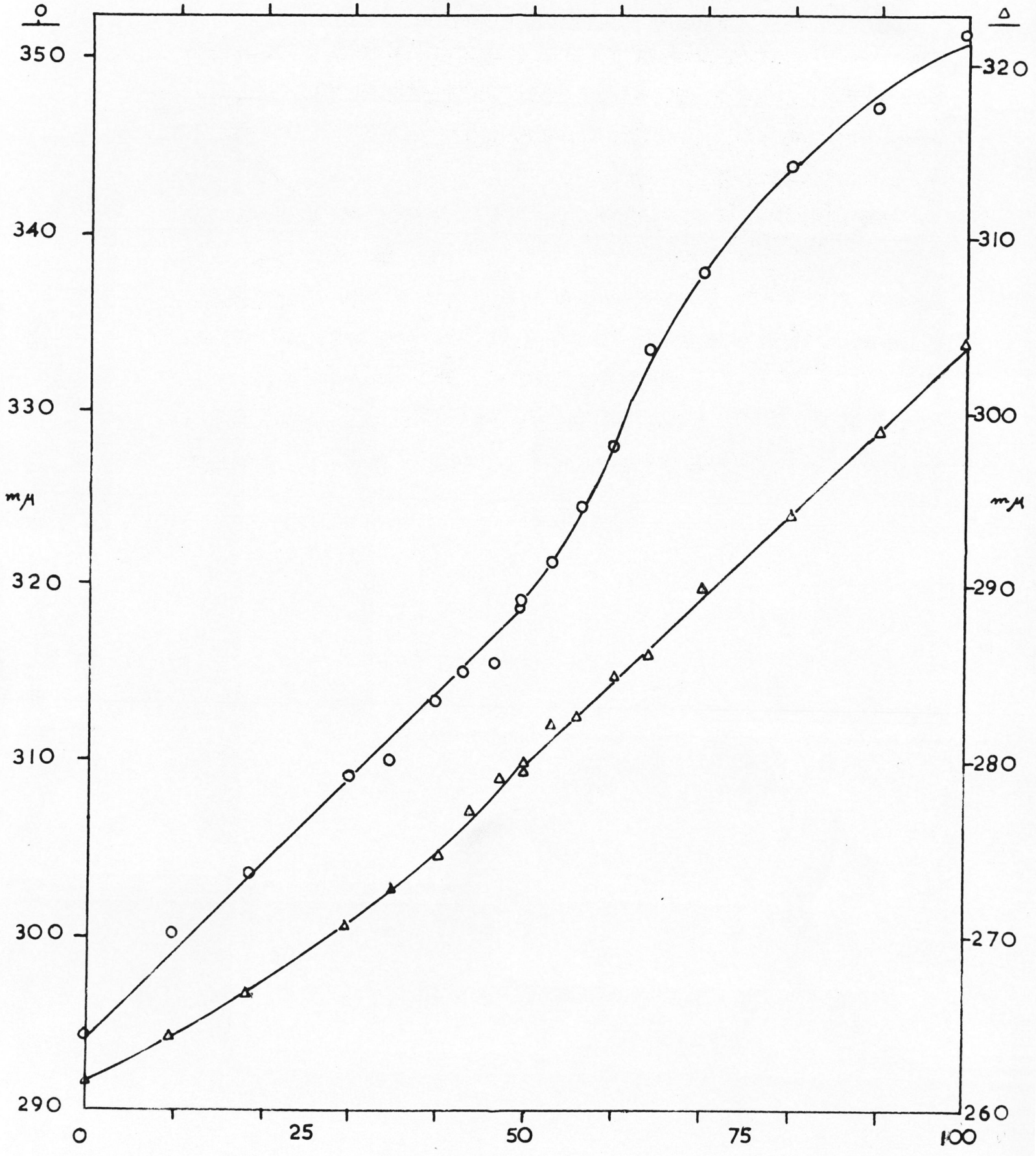
Table 47.

Absorption Maxima (mμ) in $PbBr_2/PbCl_2$ System.

Mole % $PbBr_2$	First Max.	Second Max.
0.0	293 ± 2	261.5 ± 2
10.0	300 ± 2	264 ± 1
18.3	303.5 ± 2	266.5 ± 2
30.0	309 ± 2	270.5 ± 1
34.6	310 ± 1	272.5 ± 1
40.0	313.5 ± 2	274.5 ± 1
43.0	315 ± 1	277 ± 1
47.0	316 ± 1	279 ± 1
49.9	319 ± 2	280 ± 2
50.0	318.5 ± 2	279 ± 2
53.0	321.5 ± 1	282 ± 1
56.0	324.5 ± 2	282.5 ± 1
60.0	328 ± 3	285 ± 1
64.1	333.5 ± 1	286 ± 2
70.2	328 ± 2	290 ± 1
79.6	344 ± 2	294 ± 2
90.1	347.5 ± 2	299 ± 3
100.0	352 ± 2	304 ± 3

FIGURE 42

ABSORPTION MAXIMA OF $PbCl_2/PbBr_2$



The composition plot of these features is given in Fig. 42. For the first maximum a sharp break in the plot occurs at 50% $PbBr_2$, the portion from 0-50% being linear and for the second, though a break from linearity occurs, it is difficult to locate accurately, the portion from 50-100% $PbBr_2$ being linear in this case.

The absorption bands of $PbBr_2$ and $PbCl_2$ have not been accounted for theoretically: this is hardly surprising in view of the complexity of the problem, each Pb^{++} ion being associated with 9 halogen ions at differing distances. It is impossible, therefore, in this work to account for the linearity in the range 0-50% $PbBr_2$ for the first maximum and from 50-100% $PbBr_2$ for the second, but the break at 50% $PbBr_2$, particularly at the first maximum, provides further evidence for the formation of PbClBr.

Conclusion and Discussion.

The conclusions drawn from the reflectance spectrophotometric studies are summarised. Brief discussions are given on the interpretation of the positions of the absorption maxima in the molybdates, on the oxides which do and do not react with MoO_3 to form molybdates, and on the poor results obtained in the transition metal oxide - MoO_3 systems.

The reflectance method presented for the analysis of solid mixtures depends on the attainment of a limiting absorption on grinding. For the systems investigated, excepting the lead halide - potassium halide mixtures in which reactions were shown to take place, this was achieved.

The most of the mixtures investigated the empirical equation $W = K\left(\frac{A}{R}\right)^{1\cdot383}$ held accurately over the absorption range 30-70%, which is the most useful for quantitative work. Attempts to relate the absorption or the reflectance to the percentage of an absorbing species in a mechanical mixture of solids from fundamental considerations met with no success; the number of variables which must be taken into account is very large and it is not surprising that the simple Kubelka-Munk treatment is not applicable. However, for the Al_2O_3-ZnO system, in which the ZnO is adsorbed on the surface of the alumina the Kubelka-Munk function is applicable.

For the quantitative analysis of a simple mixture of two solids a plot of % absorption against concentration could well be used as a calibration plot but, for mixtures containing more than one absorbing species, it is essential to use the additive absorption function, $\left(\frac{A}{R}\right)^{1\cdot383}$; calibration /

calibration data can conveniently be expressed in the form of simultaneous equations. The accuracy of this direct reflectance method is about 6% and though improvement is possible if the internal standard principle is adopted it is doubtful if the additional time spent is justifiable for most purposes. The reflectance method has the advantages over the x-ray method that it can be applied to amorphous as well as crystalline substances and that quantitative estimation of a low percentage, often of the order 1%, of one substance in a mixture is possible. The main disadvantage is that since the spectrum of a compound depends on its previous history, calibration data will generally only hold for samples from the same source as the standards.

The advantages of the reflectance method in detecting and estimating a small amount of one substance in a mixture of solids were put to use in the determination of the compositions of products formed in reactions between inorganic oxides, both in the solid state and on fusion. In general the method proved very satisfactory though in certain cases anomolous absorptions were obtained and these are later discussed. Table 48 gives a summary of the results obtained for the systems investigated, all of which were also studied by the x-ray method.

Table 48.

Systems studied by the Reflectance Method

System $M_xO_y - MoO_3$	Molar Ratio $\frac{M_xO_y}{MoO_3}$		Compounds
	Reflectance	X-ray	
$ZnO - MoO_3$	1·00 ± 0·01	1·0 ± 0·3	$ZnMoO_4$
$CdO - MoO_3$	1·01 ± 0·02	1·0 ± 0·3	$CdMoO_4$
$CuO - MoO_3$	*	1·0 ± 0·3	$CuMoO_4$
$NiO - MoO_3$	*	1·0 ± 0·3	$NiMoO_4$
$CoO - MoO_3$	*	1·0 ± 0·3	$CoMoO_4$
$MgO - MoO_3$	R	R	not detd.
$ThO_2 - MoO_3$	0·5	≙ 0·5	$Th(MoO_4)_2$
$ZrO_2 - MoO_3$	0·5	≙ 0·5	$Zr(MoO_4)_2$
$SiO_2 - MoO_3$	N.R.	N.R.	
$GeO_2 - MoO_3$	N.R.	N.R.	
$SnO_2 - MoO_3$	N.R.	N.R.	
$B_2O_3 - MoO_3$	N.R.	N.R.	
$Al_2O_3 - MoO_3$	0·33	*	$Al_2(MoO_4)_3$
	≙ 1·00	*	$Al_2O_3.MoO_3$
$PbO - MoO_3$ (fusion)	1·02 ± 0·03	≙ 1	$PbMoO_4$
	2·05 ± 0·04	≙ 2	$2\,PbO.MoO_3$
	5·05 ± 0·05	5·0 ± 1·1	$5\,PbO.MoO_3$
$Bi_2O_3 - MoO_3$ (fusion)	11 cmpds from 44 ± 4 to ≙ ~~0·67~~ 0·33	*	44 $Bi_2O_3.MoO_3$ to $Bi_2(MoO_4)_3$

* Method not applicable.

R. reaction but product not detd.

N.R. no reaction.

In the diffuse reflectance spectra of the products in which the cation did not have incomplete d shells the absorption maxima shown in Table 49 were observed.

Table 49.

Absorption Maxima Observed.

Compound	Maximum
$ZnMoO_4$	265mμ
$CdMoO_4$	312mμ
$MgMoO_4$	260mμ
$Th(MoO_4)_2$	275mμ
$Zr(MoO_4)_2$	295mμ
$Al_2(MoO_4)_3$	270mμ
$Al_2O_3.MoO_3$	250mμ
$PbMoO_4$	335mμ
$2PbO.MoO_3$	310mμ
$5PbO.MoO_3$	365mμ

The spectra are of the same type with one continuous absorption band in the ultraviolet. For the normal molybdates it has been reported that the absorption is associated with the molybdate ion (Kroger, 1948). Dunn (1960) says that the spectra of the anions $XO_4^=$ appear to be due to the transference of an oxygen π electron to the central ion σ orbital. Attempts to correlate the position of the absorption maximum with the nature of the cation must take into account the exact cation environment and, since the structures are unknown in most cases, this was not possible.

The spectra of the molybdates of the transition metals with incomplete d. shells are of a different type in which absorption maxima in the visible and near infra-red were observed arising from d-d transitions within the metal ion.

As regards the formation of the molybdates of the tetravalent cations in the solid state it is interesting to note that though the molybdates of zirconium (IV) and thorium (IV) are formed those of silicon (IV), germanium (IV), and tin (IV) are not. Stannic molybdate has, however, been prepared as a gel. Ostroff (1959) studied the temperatures at which the anhydrous sulphates of divalent cations decompose and related the stability of the sulphate to the ionic radius (r) and the electronegativity (s) of the cation; the higher the ratio $\frac{r}{s}$ the more stable the sulphate. Such a procedure would appear applicable for accounting for the existence of only certain of the molybdates of the tetravalent cations and in Table 50, the ratio $\frac{r}{s}$, where r is the Goldschmit empirical crystal radius of the cation and s the electronegativity on the Pauling Scale, is tabulated for the cations concerned.

Table 50.

Metal	r	s	$\frac{r}{s}$
Zr	0·87	1·4	0·62
Th	1·02	1·3	0·79
Si	0·39	1·8	0·22
Ce	0·44	1·8	0·24
Sn	0·74	1·8	0·41

The highest values of $\frac{r}{s}$ are for zirconium and thorium suggesting that they form the most stable oxysalts. The existence of the hydrated stannic molybdate and not the anhydrous can be understood if it is assumed that the hydrated salt contains hydrated cations: the effective ionic size of the cation is increased and its polarising power thereby decreased.

The reflectance method of determining compound composition was unsatisfactory for the molybdates of the transition metals having incomplete d electron shells. The spectral features arise from the d-d transitions due to the ligand field surrounding the metal ion which causes a splitting of the degenerate orbitals of an isolated ion. Consequently, the intensity of theabsorption is highly dependent on the environment of the metal ion and it is suggested that it is this which gives rise to the anomolous results obtained. Two quite distinct absorption effects were observed, the first being concerned with the absorption of the molybdate and the second with the absorption of the transition metal oxide when in excess.

For an equimolar mixture of CuO and MoO_3 on prolonged heating the absorption of the $CuMoO_4$ formed, decreased. On heating the equimolar mixture for fixed periods at various temperatures the absorption of the product was found to be the lower, the higher the temperature. Since the quality of the x-ray powder photographs improved if the preparation was carried out at relatively high temperatures (e.g. 6 lines observed in 600° product and 27 lines in 750° product) strong absorption would appear to be associated with poor crystallinity. For a series of mixtures of differing composition, reacted under identical conditions, the expected linearity of absorption with concentration /

concentration was observed in the 0-50% CuO region but not in the 50-100% region, where the absorption of the product was always higher than anticipated; it is therefore tentatively suggested that the crystallisation of the $CuMoO_4$ is inhibited by the presence of excess CuO. Similar conclusions are drawn for the NiO/MoO_3 system.

For the unsintered CuO/MoO_3 series quite different absorption changes were observed at wavelengths at which the excess CuO absorbs strongly. Later work showed that the absorption of pure CuO on heating to 1000° decreased by a factor of about 15. At 700-750° though the absorption of the pure CuO was not changed on prolonged heating when in admixture with $CuMoO_4$, it decreased. The relative difference between the observed and expected absorptions was greatest for mixtures containing only a slight CuO excess and it is therefore suggested that in the presence of $CuMoO_4$ premature sintering of the CuO takes place.

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ABSTRACT of THESIS.

The factors affecting the reflectance of an absorbing substance mixed with material not absorbing at the wavelength of measurement were investigated, and it was found that the effect of particle size could be eliminated by prolonged grinding. It is shown that the percentage by weight of an absorbing substance is directly proportional to the quantity $(\frac{A}{R})^{1.383}$ (R = percentage reflectance; A = 100 - R) and that this quantity is additive for two absorbing substances. A method is developed for the accurate determination of low concentrations of one and two absorbing substances mixed with a non-absorbing substance. However, since the spectra of inorganic compounds are dependent on their previous history the method is only applicable for mixtures from a similar source, or which have undergone similar treatment, to the standards. The method is not applicable if there is physical interaction between the components of the mixture.

The reflectance method of quantitative analysis of solid mixtures is applied to the determination of the composition of the solid products formed in solid/solid inorganic reactions: the principles involved are analogous to those used by Job in solution spectrophotometry. The method was tested by applying it to several MoO_3/basic oxide systems which had been previously studied by other techniques and then applied to other MoO_3/basic oxide systems hitherto not investigated or on which controversy exists. In all cases confirmation was obtained by a parallel x-ray powder diffraction study. For reactions involving the oxides of the non-transition metals the compositions of the products formed can

can be located within very narrow limits by the reflectance method and this becomes of greatest importance when dealing with compounds of an unbalanced composition (a compound formed from unusual molar proportions of reactants, e.g. 7:5 or 12:1). For reactions involving the transition metal oxides the reflectance method is not applicable and this is related to the nature of the spectra involved in these cases.

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